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G03F 7/004  
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H01L 21/027

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(21)Application number : 2000-402245

(71)Applicant : FUJI PHOTO FILM CO LTD

(22)Date of filing : 28.12.2000

(72)Inventor : SATO KENICHIRO

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(54) POSITIVE TYPE PHOTORESIST COMPOSITION FOR EXPOSURE WITH FAR ULTRAVIOLET RAY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a positive type photoresist composition for exposure with far UV having superior sensitivity in the resolution of contact holes in the production of a semiconductor device, capable of preventing the occurrence of particles in the dissolution of solid components in a solvent or during storage with time and capable of also preventing a variation of sensitivity due to storage with time.

SOLUTION: The positive type photoresist composition contains a compound which generates an acid when irradiated with active rays or radiation, a resin having a specified structure and a velocity of dissolution in an alkali developing solution increased by the action of the acid and a specified mixed solvent.

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**LEGAL STATUS**

[Date of request for examination]

21.11.2005

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examiner's decision of rejection or application  
converted registration]

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\* NOTICES \*

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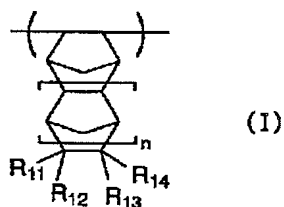
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- 3.In the drawings, any words are not translated.

## CLAIMS

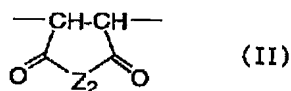
[Claim(s)]

[Claim 1] (A) The compound which generates an acid by the exposure of an activity beam of light or a radiation, the repeat structural unit shown by the (B) following general formula (I), The repeat structural unit shown by the general formula (II) and the repeat structure shown by the general formula (III) are included. The resin which the dissolution rate to an alkali developer increases according to an operation of an acid, and the partially aromatic solvent containing at least one sort chosen from a (C) following solvent A group, and at least one sort chosen from a following solvent B group, Or the partially aromatic solvent A group:propylene glycol monoalkyl ether alkoxylate B group containing at least one sort chosen from a solvent A group, and at least one sort chosen from a following solvent C group : Propylene glycol monoalkyl ether, Lactic-acid alkyl and an alkoxy propionic-acid alkyl C group: The positive type photoresist constituent for far-ultraviolet-rays exposure characterized by containing gamma-butyrolactone, ethylene carbonate, and propylene carbonate.

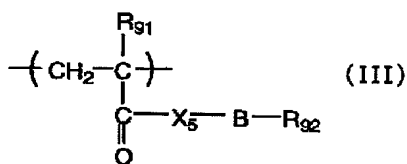
[Formula 1]



[Formula 2]



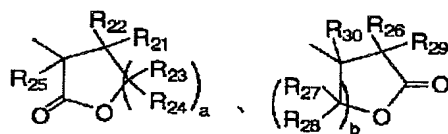
[Formula 3]



Inside of a general formula (I): R11–R14 express respectively the radical independently decomposed according to an operation of an acid, a hydrogen atom, a halogen atom, a cyano group, –COOH, –COOR15, –C(=O)–X–A–R16, an alkyl group, or a cyclic–hydrocarbon radical, and at least one of R11–R14 expresses the radical decomposed according to an operation of an acid. Moreover, at least two of R11–R14 may join together, and a ring may be formed. n expresses 0 or 1. Here, R15 expresses an alkyl group, a cyclic–hydrocarbon radical, or the –Y following sets. X expresses an oxygen atom, a sulfur atom, –NH–, –NHSO2–, or –NHSO2NH–. A expresses the combination of independent [ which is chosen from the group which consists of single bond, an alkylene group, a cyclo alkylene group, a ether group, a thioether radical, a carbonyl group, and an ester group ], or two radicals or more. R16 expresses –COOH, –COOR15, –CN, a hydroxyl group, an alkoxy group, –CO–NH–R17, –CO–NH–SO2–R17, or the –Y following sets. R17 expresses an alkyl group or a cyclic–hydrocarbon radical.

– Y sets;

[Formula 4]

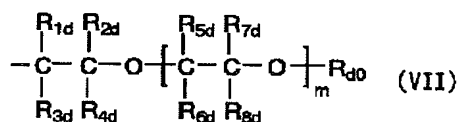
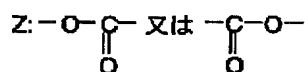
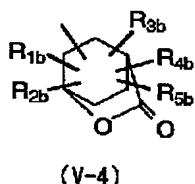
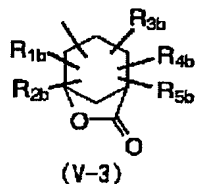
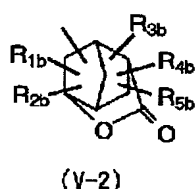
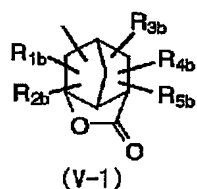
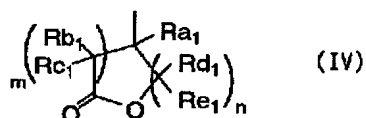


– R21–R30 express a hydrogen atom or an alkyl group independently respectively among Y sets. a and b express 1 or 2.

Inside of a general formula (II): Z2 expresses –O– or –N(R41)–. R41 expresses a hydrogen atom, a hydroxyl group, an alkyl group, a halo alkyl group, or –OSO2–R42 here. R42 expresses an alkyl group, a halo alkyl group, a cycloalkyl radical, or camphor residue.

Inside of a general formula (III): R91 expresses a hydrogen atom, low-grade alkyl group, and halogen atom or –CN. X5 expresses –O–, –S–, –NR93–, or –NR93SO2–. R93 expresses a hydrogen atom, the shape of a chain, and an annular alkyl group. B expresses single bond or a connection radical. R92 expresses the radical expressed with either a hydrogen atom, the shape of a chain, an annular alkyl group, an alkoxy group, a hydroxyl group, a carboxy group, a cyano group, –COOR94 or following general formula (IV)– (X). R94 expresses a hydrogen atom or the shape of a chain, and an annular alkyl group.

[Formula 5]



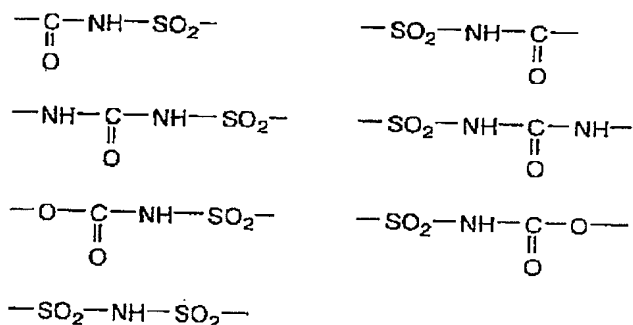
– N+ (R95) (R96) (R97) and X– (VIII)

–R98–A50–R99 (IX)

–SO3R100 (X)

In a formula (IV), Ra1, Rb1, Rc1, Rd1, and Re1 express a hydrogen atom or the alkyl group of carbon numbers 1–4 independently respectively. m and n express the integer of 0–3 independently respectively, and m+n is six or less [ 2 or more ]. In formula (V-1) – (V-4), R1 b–R5b expresses a hydrogen atom, an alkyl group, a cycloalkyl radical, or an alkenyl radical independently respectively. Two of R1 b–R5b may form a ring unitedly. In a formula (VII), R1 d–R8d expresses a hydrogen atom or an alkyl group independently respectively. Rd0 expresses a hydrogen atom, the shape of a chain, an annular alkyl group, an aryl group, or an aralkyl radical. m expresses the integer of 1–10. R95–R97 express a hydrogen atom, shape of chain, annular alkyl group, and alkenyl radical, an aryl group, or an aralkyl radical independently respectively among a formula (VIII). However, it may join together mutually and R95–R97 may form a non-ring and a ring. X– expresses R–SO3–. R expresses an aliphatic hydrocarbon radical or an aromatic hydrocarbon radical. R98 expresses single bond, an alkylene group, an arylene radical, or the divalent radical that combined these among a formula (IX). A50 expresses either of the functional groups shown below.

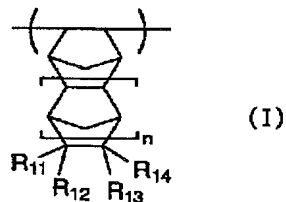
[Formula 6]



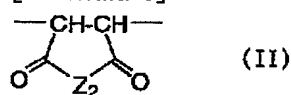
R99 expresses a hydrogen atom or an alkyl group. R100 expresses the shape of a chain, an annular alkyl group, an aryl group, or an aralkyl radical among a formula (X).

[Claim 2] (A) The compound which generates an acid by the exposure of an activity beam of light or a radiation, the repeat structural unit shown by the (B) following general formula (I), The repeat structural unit shown by the general formula (II) and the repeat structure shown by the general formula (III) are included. The resin which the dissolution rate to an alkali developer increases according to an operation of an acid, and at least one sort chosen from a (C) following solvent A group, and at least one sort chosen from a following solvent B group, And the partially aromatic solvent A group: propylene glycol monoalkyl ether alkoxylate B group containing at least one sort chosen from a following solvent C group : Propylene glycol monoalkyl ether, Lactic-acid alkyl and an alkoxy propionic-acid alkyl C group: The positive type photoresist constituent characterized by containing gamma-butyrolactone, ethylene carbonate, and propylene carbonate.

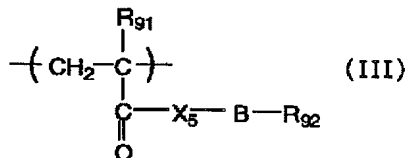
[Formula 7]



[Formula 8]



[Formula 9]

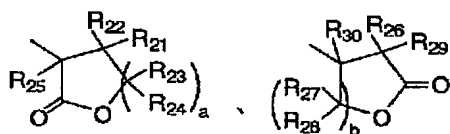


Inside of a general formula (I): R11–R14 express respectively the radical independently decomposed according to an operation of an acid, a hydrogen atom, a halogen atom, a cyano group, –COOH, –COOR15, –C(=O)–X–A–R16, an alkyl group, or a cyclic-hydrocarbon radical, and at least one of R11–R14 expresses

the radical decomposed according to an operation of an acid. Moreover, at least two of R11–R14 may join together, and a ring may be formed. n expresses 0 or 1. Here, R15 expresses an alkyl group, a cyclic-hydrocarbon radical, or the –Y following sets. X expresses an oxygen atom, a sulfur atom, –NH–, –NHSO<sub>2</sub>–, or –NHSO<sub>2</sub>NH–. A expresses the combination of independent [ which is chosen from the group which consists of single bond, an alkylene group, a cyclo alkylene group, a ether group, a thioether radical, a carbonyl group, and an ester group ], or two radicals or more. R16 expresses –COOH, –COOR15, –CN, a hydroxyl group, an alkoxy group, –CO–NH–R17, –CO–NH–SO<sub>2</sub>–R17, or the –Y following sets. R17 expresses an alkyl group or a cyclic-hydrocarbon radical.

– Y sets;

[Formula 10]

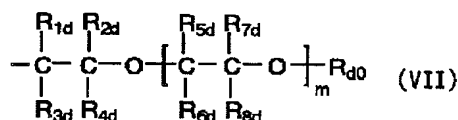
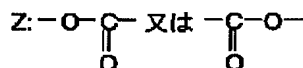
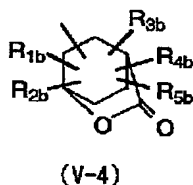
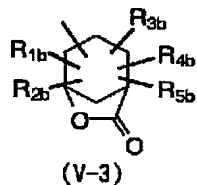
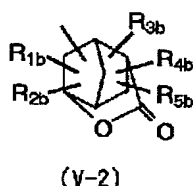
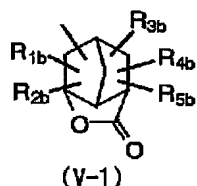
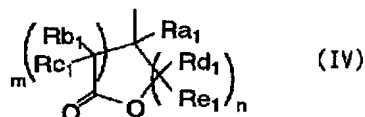


– R21–R30 express a hydrogen atom or an alkyl group independently respectively among Y sets. a and b express 1 or 2.

Inside of a general formula (II): Z2 expresses –O– or –N(R41)–. R41 expresses a hydrogen atom, a hydroxyl group, an alkyl group, a halo alkyl group, or –OSO<sub>2</sub>–R42 here. R42 expresses an alkyl group, a halo alkyl group, a cycloalkyl radical, or camphor residue.

Inside of a general formula (III): R91 expresses a hydrogen atom, low-grade alkyl group, and halogen atom or –CN. X5 expresses –O–, –S–, –NR93–, or –NR93SO<sub>2</sub>–. R93 expresses a hydrogen atom, the shape of a chain, and an annular alkyl group. B expresses single bond or a connection radical. R92 expresses the radical expressed with either a hydrogen atom, the shape of a chain, an annular alkyl group, an alkoxy group, a hydroxyl group, a carboxy group, a cyano group, –COOR94 or following general formula (IV)– (X). R94 expresses a hydrogen atom or the shape of a chain, and an annular alkyl group.

[Formula 11]



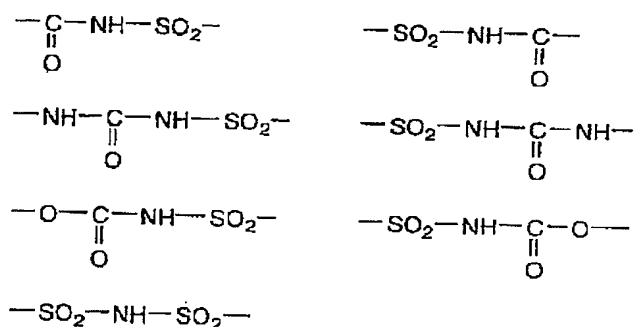
- N+ (R95) (R96) (R97) and X- (VIII)

-R98-A50-R99 (IX)

-SO3R100 (X)

In a formula (IV), Ra1, Rb1, Rc1, Rd1, and Re1 express a hydrogen atom or the alkyl group of carbon numbers 1-4 independently respectively. m and n express the integer of 0-3 independently respectively, and m+n is six or less [ 2 or more ]. In formula (V-1) - (V-4), R1 b-R5b expresses a hydrogen atom, an alkyl group, a cycloalkyl radical, or an alkenyl radical independently respectively. Two of R1 b-R5b may form a ring unitedly. In a formula (VII), R1 d-R8d expresses a hydrogen atom or an alkyl group independently respectively. Rd0 expresses a hydrogen atom, the shape of a chain, an annular alkyl group, an aryl group, or an aralkyl radical. m expresses the integer of 1-10. R95-R97 express a hydrogen atom, shape of chain, annular alkyl group, and alkenyl radical, an aryl group, or an aralkyl radical independently respectively among a formula (VIII). However, it may join together mutually and R95-R97 may form a non-ring and a ring. X- expresses R-SO3-. R expresses an aliphatic hydrocarbon radical or an aromatic hydrocarbon radical. R98 expresses single bond, an alkylene group, an arylene radical, or the divalent radical that combined these among a formula (IX). A50 expresses either of the functional groups shown below.

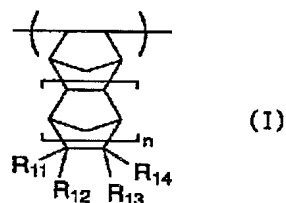
[Formula 12]



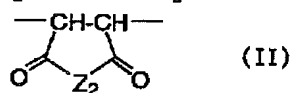
R99 expresses a hydrogen atom or an alkyl group. R100 expresses the shape of a chain, an annular alkyl group, an aryl group, or an aralkyl radical among a formula (X).

[Claim 3] (A) The compound which generates an acid by the exposure of an activity beam of light or a radiation, the repeat structural unit shown by the (B) following general formula (I), including the repeat structural unit shown by the general formula (II), and the repeat structure shown by the general formula (III), among the resin which the dissolution rate to an alkali developer increases according to an operation of an acid, and (C) lactic-acid alkyl At least one sort, The positive type photoresist constituent for far-ultraviolet-rays exposure characterized by containing the partially aromatic solvent containing at least one sort in an ester solvent and alkoxy propionic-acid alkyl.

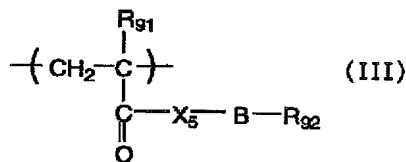
[Formula 13]



[Formula 14]



[Formula 15]



– R21–R30 express a hydrogen atom or an alkyl group independently respectively among Y sets. a and b express 1 or 2.

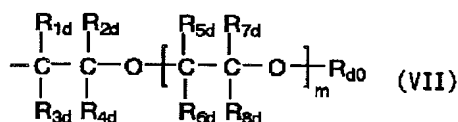
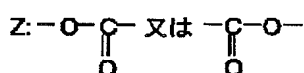
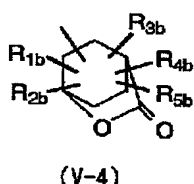
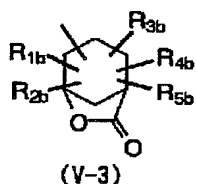
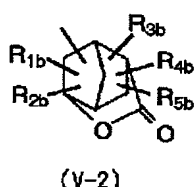
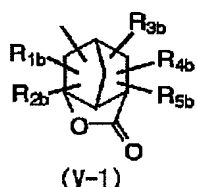
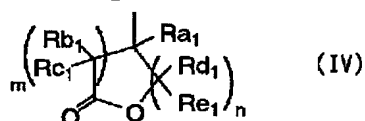
Inside of a general formula (II): Z2 expresses –O– or –N(R41)–. R41 expresses a hydrogen atom, a hydroxyl group, an alkyl group, a halo alkyl group, or –OSO2–R42 here. R42 expresses an alkyl group, a halo alkyl group, a cycloalkyl radical, or camphor residue.

Inside of a general formula (III): R91 expresses a hydrogen atom, low-grade alkyl group, and halogen atom or



-CN. X5 expresses -O-, -S-, -NR<sub>93</sub>-, or -NR<sub>93</sub>SO<sub>2</sub>-. R<sub>93</sub> expresses a hydrogen atom, the shape of a chain, and an annular alkyl group. B expresses single bond or a connection radical. R<sub>92</sub> expresses the radical expressed with either a hydrogen atom, the shape of a chain, an annular alkyl group, an alkoxy group, a hydroxyl group, a carboxy group, a cyano group, -COOR<sub>94</sub> or following general formula (IV)-(X). R<sub>94</sub> expresses a hydrogen atom or the shape of a chain, and an annular alkyl group.

[Formula 16]



- N+ (R<sub>95</sub>) (R<sub>96</sub>) (R<sub>97</sub>) and X- (VIII)

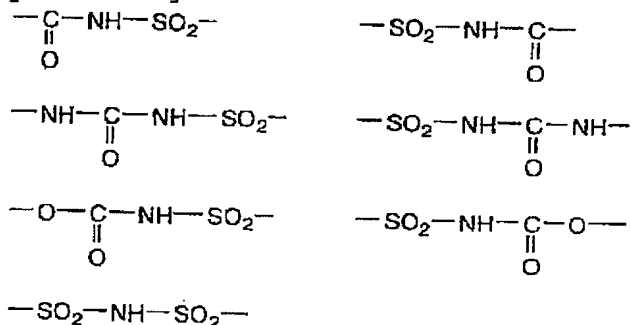
-R<sub>98</sub>-A<sub>50</sub>-R<sub>99</sub> (IX)

-SO<sub>3</sub>R<sub>100</sub> (X)

In a formula (IV), Ra<sub>1</sub>, Rb<sub>1</sub>, Rc<sub>1</sub>, Rd<sub>1</sub>, and Re<sub>1</sub> express a hydrogen atom or the alkyl group of carbon numbers 1-4 independently respectively. m and n express the integer of 0-3 independently respectively, and m+n is six or less [ 2 or more ]. In formula (V-1) - (V-4), R<sub>1b</sub>-R<sub>5b</sub> expresses a hydrogen atom, an alkyl group, a cycloalkyl radical, or an alkenyl radical independently respectively. Two of R<sub>1b</sub>-R<sub>5b</sub> may form a ring unitedly. In a formula (VII), R<sub>1d</sub>-R<sub>8d</sub> expresses a hydrogen atom or an alkyl group independently respectively. Rd<sub>0</sub> expresses a hydrogen atom, the shape of a chain, an annular alkyl group, an aryl group, or an aralkyl radical. m expresses the integer of 1-10. R<sub>95</sub>-R<sub>97</sub> express a hydrogen atom, shape of chain, annular alkyl group, and

alkenyl radical, an aryl group, or an aralkyl radical independently respectively among a formula (VIII). However, it may join together mutually and R95-R97 may form a non-ring and a ring. X- expresses R-SO<sub>3</sub>-. R expresses an aliphatic hydrocarbon radical or an aromatic hydrocarbon radical. R98 expresses single bond, an alkylene group, an arylene radical, or the divalent radical that combined these among a formula (IX). A50 expresses either of the functional groups shown below.

[Formula 17]

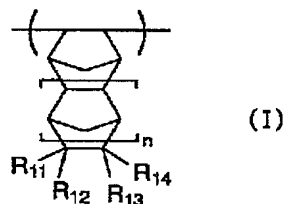


R99 expresses a hydrogen atom or an alkyl group. R100 expresses the shape of a chain, an annular alkyl group, an aryl group, or an aralkyl radical among a formula (X).

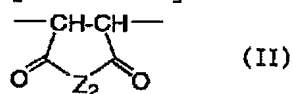
[Claim 4] The positive type photoresist constituent for far-ultraviolet-rays exposure according to claim 3 with which the solvent of (C) is characterized by containing at least one sort in gamma-butyrolactone, ethylene carbonate, and propylene carbonate further.

[Claim 5] (A) The compound which generates an acid by the exposure of an activity beam of light or a radiation, the repeat structural unit shown by the (B) following general formula (I), The repeat structural unit shown by the general formula (II) and the repeat structure shown by the general formula (III) are included. The resin which the dissolution rate to an alkali developer increases according to an operation of an acid, and the solvent of (C) The positive type photoresist constituent for far-ultraviolet-rays exposure characterized by containing at least one sort and heptanone among propylene glycol monoalkyl ether, lactic-acid alkyl, and alkoxy propionic-acid alkyl.

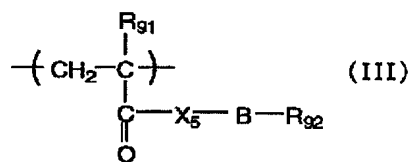
[Formula 18]



[Formula 19]



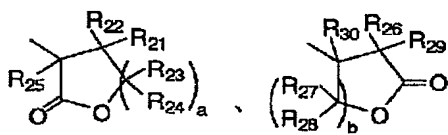
[Formula 20]



Inside of a general formula (I): R11–R14 express respectively the radical independently decomposed according to an operation of an acid, a hydrogen atom, a halogen atom, a cyano group, –COOH, –COOR15, –C(=O)–X–A–R16, an alkyl group, or a cyclic-hydrocarbon radical, and at least one of R11–R14 expresses the radical decomposed according to an operation of an acid. Moreover, at least two of R11–R14 may join together, and a ring may be formed. n expresses 0 or 1. Here, R15 expresses an alkyl group, a cyclic-hydrocarbon radical, or the –Y following sets. X expresses an oxygen atom, a sulfur atom, –NH–, –NHSO2–, or –NHSO2NH–. A expresses the combination of independent [ which is chosen from the group which consists of single bond, an alkylene group, a cyclo alkylene group, a ether group, a thioether radical, a carbonyl group, and an ester group ], or two radicals or more. R16 expresses –COOH, –COOR15, –CN, a hydroxyl group, an alkoxy group, –CO–NH–R17, –CO–NH–SO2–R17, or the –Y following sets. R17 expresses an alkyl group or a cyclic-hydrocarbon radical.

– Y sets;

[Formula 21]

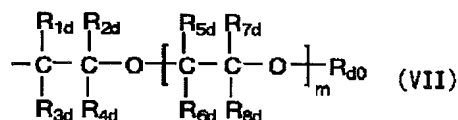
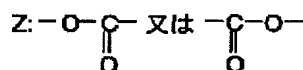
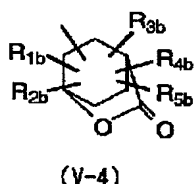
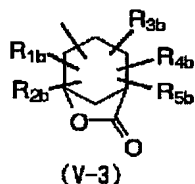
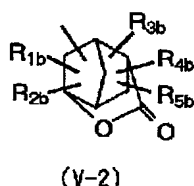
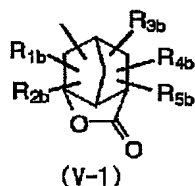
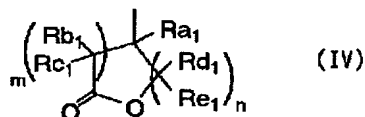


– R21–R30 express a hydrogen atom or an alkyl group independently respectively among Y sets. a and b express 1 or 2.

Inside of a general formula (II): Z2 expresses –O– or –N(R41)–. R41 expresses a hydrogen atom, a hydroxyl group, an alkyl group, a halo alkyl group, or –OSO2–R42 here. R42 expresses an alkyl group, a halo alkyl group, a cycloalkyl radical, or camphor residue.

Inside of a general formula (III): R91 expresses a hydrogen atom, low-grade alkyl group, and halogen atom or –CN. X5 expresses –O–, –S–, –NR93–, or –NR93SO2–. R93 expresses a hydrogen atom, the shape of a chain, and an annular alkyl group. B expresses single bond or a connection radical. R92 expresses the radical expressed with either a hydrogen atom, the shape of a chain, an annular alkyl group, an alkoxy group, a hydroxyl group, a carboxy group, a cyano group, –COOR94 or following general formula (IV)– (X). R94 expresses a hydrogen atom or the shape of a chain, and an annular alkyl group.

[Formula 22]



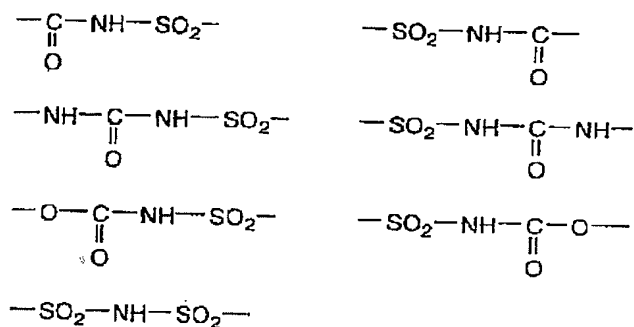
- N+ (R95) (R96) (R97) and X- (VIII)

-R98-A50-R99 (IX)

-SO3R100 (X)

In a formula (IV), Ra1, Rb1, Rc1, Rd1, and Re1 express a hydrogen atom or the alkyl group of carbon numbers 1-4 independently respectively. m and n express the integer of 0-3 independently respectively, and m+n is six or less [ 2 or more ]. In formula (V-1) - (V-4), R1 b-R5b expresses a hydrogen atom, an alkyl group, a cycloalkyl radical, or an alkenyl radical independently respectively. Two of R1 b-R5b may form a ring unitedly. In a formula (VII), R1 d-R8d expresses a hydrogen atom or an alkyl group independently respectively. Rd0 expresses a hydrogen atom, the shape of a chain, an annular alkyl group, an aryl group, or an aralkyl radical. m expresses the integer of 1-10. R95-R97 express a hydrogen atom, shape of chain, annular alkyl group, and alkenyl radical, an aryl group, or an aralkyl radical independently respectively among a formula (VIII). However, it may join together mutually and R95-R97 may form a non-ring and a ring. X- expresses R-SO3-. R expresses an aliphatic hydrocarbon radical or an aromatic hydrocarbon radical. R98 expresses single bond, an alkylene group, an arylene radical, or the divalent radical that combined these among a formula (IX). A50 expresses either of the functional groups shown below.

[Formula 23]

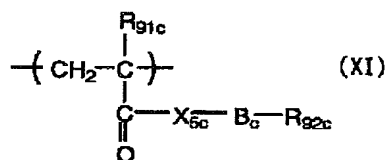


R99 expresses a hydrogen atom or an alkyl group. R100 expresses the shape of a chain, an annular alkyl group, an aryl group, or an aralkyl radical among a formula (X).

[Claim 6] The positive type photoresist constituent for far-ultraviolet-rays exposure according to claim 5 with which the solvent of (C) is characterized by containing at least one sort in gamma-butyrolactone, ethylene carbonate, and propylene carbonate further.

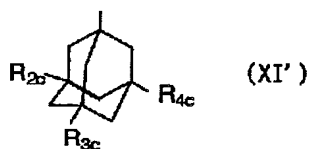
[Claim 7] (B) The positive type photoresist constituent for far-ultraviolet-rays exposure according to claim 1 to 6 characterized by the resin of a component containing the repeat unit further expressed with the following type (XI).

[Formula 24]



Inside of a general formula (XI): R91c expresses a hydrogen atom, low-grade alkyl group, and halogen atom or -CN. X5c expresses -O-, -S-, -NR93c-, or -NR93cSO2-. R93c expresses a hydrogen atom, the shape of a chain, and an annular alkyl group. Bc expresses single bond or a connection radical. R92c expresses the radical expressed with the following general formula (XI').

[Formula 25]



In a general formula (XI'), R2c-R4c expresses a hydrogen atom or a hydroxyl group independently respectively. However, at least one of R2c-R4c expresses a hydroxyl group.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the positive type photoresist constituent for far-ultraviolet-rays exposure used for super-micro lithography processes, such as a VLSI and manufacture of a high capacity microchip, or other photofabrication processes. Furthermore, it is related with the positive type photoresist constituent for far-ultraviolet-rays exposure which can form in detail the far-ultraviolet-rays field containing excimer laser light, and the pattern especially made highly minute using light with a wavelength of 250nm or less.

[0002]

[Description of the Prior Art] in recent years, the integrated circuit is raising the degree of integration increasingly, and consists of the line breadth below a half micron in manufacture of semi-conductor substrates, such as a VLSI, -- processing of a detailed pattern has overly come to be needed. In order to fulfill the need, operating wavelength of the aligner used for photolithography is short-wave-ized increasingly, and by the time using the excimer laser light (XeCl, KrF, ArF, etc.) of short wavelength also in far ultraviolet rays is now examined, it will become. A chemistry multiplier system resist is one of those are used for the pattern formation of the lithography in this wavelength field.

[0003] Generally a chemistry multiplier system resist can be divided roughly into three kinds, the common-name two-component system, a 2.5 component system, and 3 component system. The two-component system has combined the compound (it is henceforth called the photo-oxide generating agent) and binder resin which generate an acid by the photolysis. This binder resin is resin which has in intramolecular the radical (it is also called an acidolysis nature machine) to which an operation of an acid decomposes into and the solubility in the inside of the alkali developer of resin is made to increase. A 2.5 component system contains the low molecular weight compound which has an acidolysis nature machine further in such the two-component system. 3 component system contains a photo-oxide generating agent, alkali fusibility resin, and the above-mentioned low molecular weight compound.

[0004] Although the above-mentioned chemistry multiplier system resist is suitable for ultraviolet rays or the photoresist for an far-ultraviolet-rays exposure, it is necessary to correspond to the demand characteristics on use further in it. The photoresist constituent which combined acrylic resin with still less (meta) absorption as a photoresist constituent for the ArF light sources than the styrene resin which carried out hydroxy \*\* partially with the compound which therefore generates an acid in light is proposed. For example, there are JP,7-199467,A, 7-252324, etc. By JP,6-289615,A, the resin the 3rd class carbon organic radical carried out [ resin ] the ester bond to the oxygen of the carboxyl group of an acrylic acid is indicated especially.

[0005] Although the acidolysis nature resin which repeats acrylic ester and fumaric-acid ester and is made into a structural unit is furthermore indicated by JP,7-234511,A, a pattern profile, substrate adhesion, etc. are inadequate and the actual condition is that the satisfactory engine performance is not obtained.

[0006] In order that the lithography process which manufactures the device using a design rule (0.18 micrometers and 0.13 micrometers) may use light with a wavelength of 193nm as exposure radiation in many cases, it asks for the resist polymer which seldom contains ethylene system partial saturation nature.

[0007] Although the resin with which the alicyclic hydrocarbon part was introduced for the purpose of dry etching resistance grant is proposed as a photoresist constituent for the ArF light sources Harder [ which becomes very in canal ], a system as evil of alicyclic hydrocarbon part installation The development in the

tetramethylammonium hydroxide (henceforth, TMAH) water solution conventionally used broadly as a resist developer becomes difficult, or the phenomenon of a resist separating from a substrate in development is seen.

[0008] Although correspondence of mixing organic solvents, such as isopropyl alcohol, with a developer is considered corresponding to hydrophobing of such a resist and a temporary result is seen, it cannot necessarily be referred to as that the problem was solved that concern and the process of the swelling of the resist film become complicated etc. Many measures of compensating various canal alicyclic hydrocarbon parts with approach called amelioration of a resist by installation of a hydrophilic group are also made. Although the energy susceptibility resist ingredient containing the polymer obtained by carrying out the polymerization of the monomer which has the monomer which has alicyclic structures, such as a norbornene ring, in a principal chain, a maleic anhydride, and a carboxyl group to JP,10-10739,A is indicated, and the transparency over the wavelength of 193nm improves, when it cannot necessarily be said to be high sensitivity but the lithography after 0.13 micrometer is considered, the resist engine performance in which resolving power is insufficient etc. is insufficient.

[0009] The radiation-sensitive resin constituent containing the resin which has an alicyclic frame in a principal chain, and a radiation-sensitive acid generator is indicated by JP,10-111569,A. In JP,11-202491,A, the polymer containing a norbornene derivative and the radiation-sensitive resin constituent containing an androstane-17-carboxylate system compound are indicated.

[0010] Moreover, in JP,9-73173,A, JP,9-90637,A, and JP,10-161313,A, the alkali fusibility radical protected with the structure containing an alicyclic radical and its alkali fusibility radical \*\*\*\* with an acid, and the resist ingredient using an acid sensitivity compound including the structural unit made to serve as alkali fusibility is indicated.

[0011] Moreover, the resist constituent which contains in JP,9-90637,A, 10-207069, and a 10-274852 official report the acidolysis nature resin which has specific lactone structure is indicated. The resist of the chemistry magnification mold containing the terpolymer which has the specific repeat structural unit which has norbornene structure in a principal chain is indicated by JP,10-130340,A. The repeat structural unit which has adamantane structure in a side chain, and the resin which repeats a maleic anhydride and is contained as a structural unit are indicated by JP,11-305444,A. EP 1048983A1 is indicating the constituent containing the resin which has the repeat unit which consists of norbornene which has a specific acidolysis nature machine for the purpose of amelioration of preservation stability, transparency, dry etching nature, sensibility, resolution, a pattern configuration, etc., the repeat unit which consists of an anhydride, and the repeat unit which has an alicyclic radical.

[0012] However, these resist constituents had the problem of the sensibility fluctuation by generating of particle, or preservation with the passage of time at the time of melting solid content to a solvent, or the time of preservation with the passage of time. Moreover, in addition to these, improvement in sensibility in resolving of a contact hole was also desired.

[0013]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is in manufacture of a semiconductor device to offer the positive type photoresist constituent for far-ultraviolet-rays exposure which can prevent generating of the particle at the time of melting solid content to a solvent with the

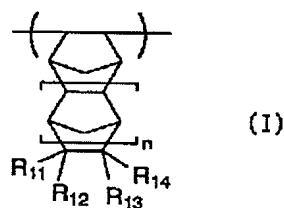
sensibility which was excellent in resolving of a contact hole, or the time of preservation with the passage of time, and can prevent fluctuation of the sensibility by preservation with the passage of time further.

[0014]

[Means for Solving the Problem] this invention person etc. resulted that the purpose of this invention was reached in a header and this invention by using specific resin and a specific specific solvent, as a result of examining wholeheartedly the component of the resist constituent in a positive type chemistry multiplier system. Namely, the compound to which the above-mentioned purpose generates an acid by the exposure of (A) activity beam of light or a radiation, And the repeat structural unit shown by the (B) following general formula (I), the repeat structural unit shown by the general formula (II), And it is attained by the resin which the dissolution rate to an alkali developer increases according to an operation of an acid, and the positive type photoresist constituent for far-ultraviolet-rays exposure characterized by containing the partially aromatic solvent of (C) specification including the repeat structure shown by the general formula (III).

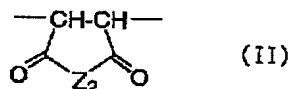
[0015]

[Formula 26]



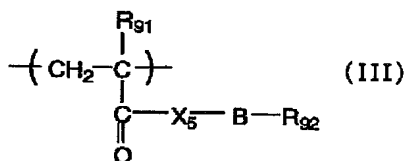
[0016]

[Formula 27]



[0017]

[Formula 28]



[0018] Inside of a general formula (I): R11-R14 express respectively the radical independently decomposed according to an operation of an acid, a hydrogen atom, a halogen atom, a cyano group, -COOH, -COOR15, -C(=O)-X-A-R16, an alkyl group, or a cyclic-hydrocarbon radical, and at least one of R11-R14 expresses the radical decomposed according to an operation of an acid. Moreover, at least two of R11-R14 may join together, and a ring may be formed. n expresses 0 or 1. Here, R15 expresses an alkyl group, a cyclic-hydrocarbon radical, or the -Y following sets. X expresses an oxygen atom, a sulfur atom, -NH-, -NHSO2-, or -NHSO2NH-. A expresses the combination of independent [ which is chosen from the group which consists of single bond, an alkylene group, a cyclo alkylene group, a ether group, a thioether radical, a

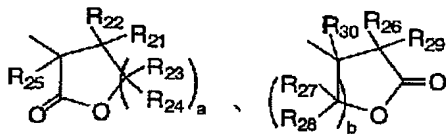


carbonyl group, and an ester group ], or two radicals or more. R16 expresses  $-\text{COOH}$ ,  $-\text{COOR15}$ ,  $-\text{CN}$ , a hydroxyl group, an alkoxy group,  $-\text{CO-NH-R17}$ ,  $-\text{CO-NH-SO}_2\text{-R17}$ , or the  $-\text{Y}$  following sets. R17 expresses an alkyl group or a cyclic-hydrocarbon radical.

- Y sets;

[0019]

[Formula 29]

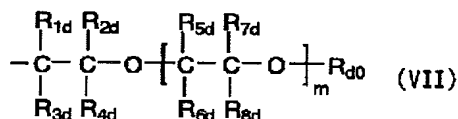
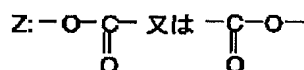
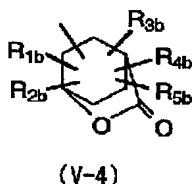
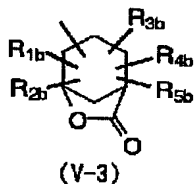
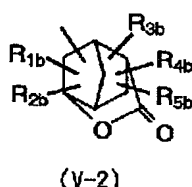
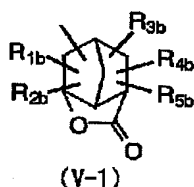
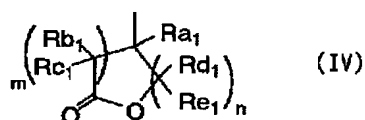


[0020] - R21-R30 express a hydrogen atom or an alkyl group independently respectively among Y sets. a and b express 1 or 2.

[0021] Inside of a general formula (II): Z2 expresses  $-\text{O}-$  or  $-\text{N(R41)}-$ . R41 expresses a hydrogen atom, a hydroxyl group, an alkyl group, a halo alkyl group, or  $-\text{OSO}_2\text{-R42}$  here. R42 expresses an alkyl group, a halo alkyl group, a cycloalkyl radical, or camphor residue.

Inside of a general formula (III): R91 expresses a hydrogen atom, low-grade alkyl group, and halogen atom or  $-\text{CN}$ . X5 expresses  $-\text{O}-$ ,  $-\text{S}-$ ,  $-\text{NR93}-$ , or  $-\text{NR93SO}_2-$ . R93 expresses a hydrogen atom, the shape of a chain, and an annular alkyl group. B expresses single bond or a connection radical. R92 expresses the radical expressed with either a hydrogen atom, the shape of a chain, an annular alkyl group, an alkoxy group, a hydroxyl group, a carboxy group, a cyano group,  $-\text{COOR94}$  or following general formula (IV)- (X). R94 expresses a hydrogen atom or the shape of a chain, and an annular alkyl group.

[0022]



[Formula 30]

[0023]

- N+ (R95) (R96) (R97) and X- (VIII)

-R98-A50-R99 (IX)

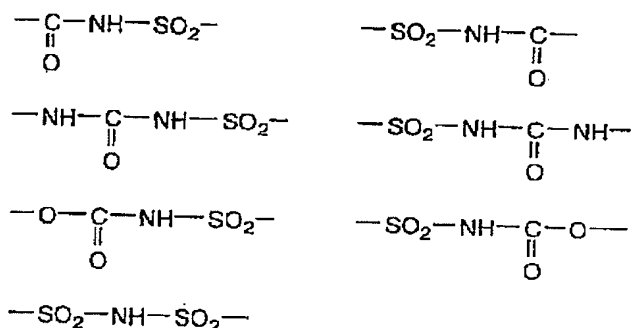
-SO3R100 (X)

[0024] In a formula (IV), Ra1, Rb1, Rc1, Rd1, and Re1 express a hydrogen atom or the alkyl group of carbon numbers 1-4 independently respectively. m and n express the integer of 0-3 independently respectively, and m+n is six or less [ 2 or more ]. In formula (V-1) - (V-4), R1 b-R5b expresses a hydrogen atom, an alkyl group, a cycloalkyl radical, or an alkenyl radical independently respectively. Two of R1 b-R5b may form a ring unitedly. In a formula (VII), R1 d-R8d expresses a hydrogen atom or an alkyl group independently respectively. Rd0 expresses a hydrogen atom, the shape of a chain, an annular alkyl group, an aryl group, or an aralkyl radical. m expresses the integer of 1-10. R95-R97 express a hydrogen atom, shape of chain, annular alkyl group, and alkenyl radical, an aryl group, or an aralkyl radical independently respectively among a formula (VIII). However, it may join together mutually and R95-R97 may form a non-ring and a ring. X- expresses R-SO3-. R expresses an aliphatic hydrocarbon radical or an aromatic hydrocarbon radical. R98 expresses single bond, an alkylene group, an arylene radical, or the divalent radical that combined these

among a formula (IX). A50 expresses either of the functional groups shown below.

[0025]

[Formula 31]



[0026] R99 expresses a hydrogen atom or an alkyl group. R100 expresses the shape of a chain, an annular alkyl group, an aryl group, or an aralkyl radical among a formula (X).

[0027] (1) The positive type photoresist constituent for far-ultraviolet-rays exposure characterized by being the partially aromatic solvent which contains at least one sort chosen from a following solvent A group, at least one sort chosen from a following solvent B group, or at least one sort chosen from a solvent A group, and at least one sort chosen from a following solvent C group in the above-mentioned configuration.

A group: -- propylene glycol monoalkyl ether alkoxylate B group: -- propylene glycol monoalkyl ether, lactic-acid alkyl and alkoxy propionic-acid alkyl C group: gamma-butyrolactone, ethylene carbonate, and propylene carbonate [0028] (2) The positive type photoresist constituent for far-ultraviolet-rays exposure characterized by being the partially aromatic solvent which contains at least one sort chosen from a (C) following solvent A group, at least one sort chosen from a following solvent B group, and at least one sort chosen from a following solvent C group in the above-mentioned configuration.

A group: -- propylene glycol monoalkyl ether alkoxylate B group: -- propylene glycol monoalkyl ether, lactic-acid alkyl and alkoxy propionic-acid alkyl C group: gamma-butyrolactone, ethylene carbonate, and propylene carbonate [0029] (3) The positive type photoresist constituent for far-ultraviolet-rays exposure characterized by being a partially aromatic solvent containing at least one sort and at least one sort in an ester solvent and alkoxy propionic-acid alkyl in (C) lactic-acid alkyl in the above-mentioned configuration.

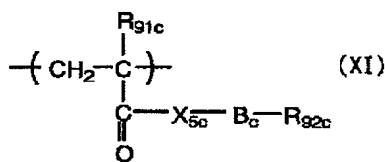
[0030] (4) The positive type photoresist constituent with which the solvent of (C) is characterized by containing content for at least one sort and heptanone further among propylene glycol monoalkyl ether, lactic-acid alkyl, and alkoxy propionic-acid alkyl in the above-mentioned configuration.

[0031] The above (3) whose solvent of (5) and (C) is characterized by containing at least one sort in gamma-butyrolactone, ethylene carbonate, and propylene carbonate further, or a positive type photoresist constituent given in (4).

[0032] (6) The positive type photoresist constituent for far-ultraviolet-rays exposure given in either of aforementioned (1) - (5) characterized by the resin of the (B) component containing the repeat unit further expressed with the following type (XI) in the above-mentioned configuration.

[0033]

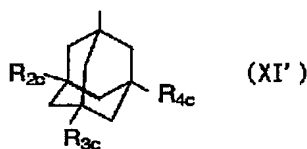
[Formula 32]



[0034] Inside of a general formula (XI): R<sub>91c</sub> expresses a hydrogen atom, low-grade alkyl group, and halogen atom or -CN. X<sub>5c</sub> expresses -O-, -S-, -NR<sub>93c</sub>-, or -NR<sub>93c</sub>SO<sub>2</sub>-. R<sub>93c</sub> expresses a hydrogen atom, the shape of a chain, and an annular alkyl group. B<sub>c</sub> expresses single bond or a connection radical. R<sub>92c</sub> expresses the radical expressed with the following general formula (XI').

[0035]

[Formula 33]



[0036] In a general formula (XI'), R<sub>2c</sub>-R<sub>4c</sub> expresses a hydrogen atom or a hydroxyl group independently respectively. However, at least one of R<sub>2c</sub>-R<sub>4c</sub> expresses a hydroxyl group.

[0037] Furthermore, the following modes are also desirable.

(7) Furthermore, a fluorine system and /\*\* are a positive type photoresist constituent for far-ultraviolet-rays exposure given in either of above-mentioned (1) - (6) characterized by containing a silicon system surfactant.

[0038] (8) The positive type photoresist constituent for far-ultraviolet-rays exposure given in either of above-mentioned (1) - (7) characterized by furthermore containing an organic base nature compound.

[0039]

[Embodiment of the Invention] Hereafter, the compound used for this invention is explained to a detail.

[0040] [1] The constituent of compound this invention which generates an acid by the exposure of (A) activity beam of light or a radiation contains the compound (photo-oxide generating agent) which generates an acid by the exposure of (A) activity beam of light or a radiation.

[0041] The compounds which generate an acid as a photo-oxide generating agent by a well-known light (400-200nm ultraviolet rays, far ultraviolet rays, especially preferably g line, h line, i line, KrF excimer laser light) currently used for the photoinitiator of optical cationic polymerization, the photoinitiator of an optical radical polymerization, the optical decolorizing agent of coloring matter, optical alterant, or a micro resist, ArF excimer laser light, the electron ray, the X-ray, the molecular beam, or the ion beam, and those mixture can be used choosing them suitably.

[0042] Moreover, the compound which is represented by onium salt, such as diazonium salt, ammonium salt, phosphonium salt, iodonium salt, sulfonium salt, a seleno NIUMU salt, and arsonium salt, an organic halogenated compound, an organic metal / organic halogenide, the photo-oxide generating agent that has o-nitrobenzyl mold protective group, imino sulfonate, etc. as a photo-oxide generating agent used for other this inventions, for example and which photodissociates and generates a sulfonic acid, a disulfon compound,

a diazo keto sulfone, a diazo disulfon compound, etc. can be mentioned. Moreover, the radical which generates an acid by such light, or the compound which introduced the compound into the principal chain or side chain of a polymer can be used.

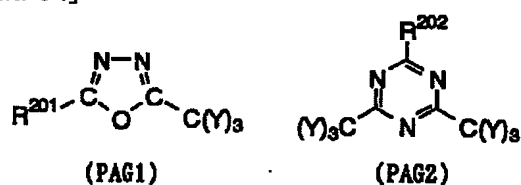
[0043] Furthermore, the compound which generates an acid by the light of a publication can also be used for V.N.R.Pillai, Synthesis, (1), 1 (1980), A.Abad et al, Tetrahedron Lett., (47) 4555 (1971), D.H.R.Barton et al, J.Chem.Soc., (C), 329 (1970), U.S. Pat. No. 3,779,778, the Europe patent No. 126,712, etc.

[0044] In the compound which generates the acid in which the above-mentioned concomitant use is possible, especially the thing used effectively is explained below.

(1) S-triazine derivative expressed with the oxazole derivative or general formula (PAG2) expressed with the following general formula (PAG1) which the trihalomethyl group permuted.

[0045]

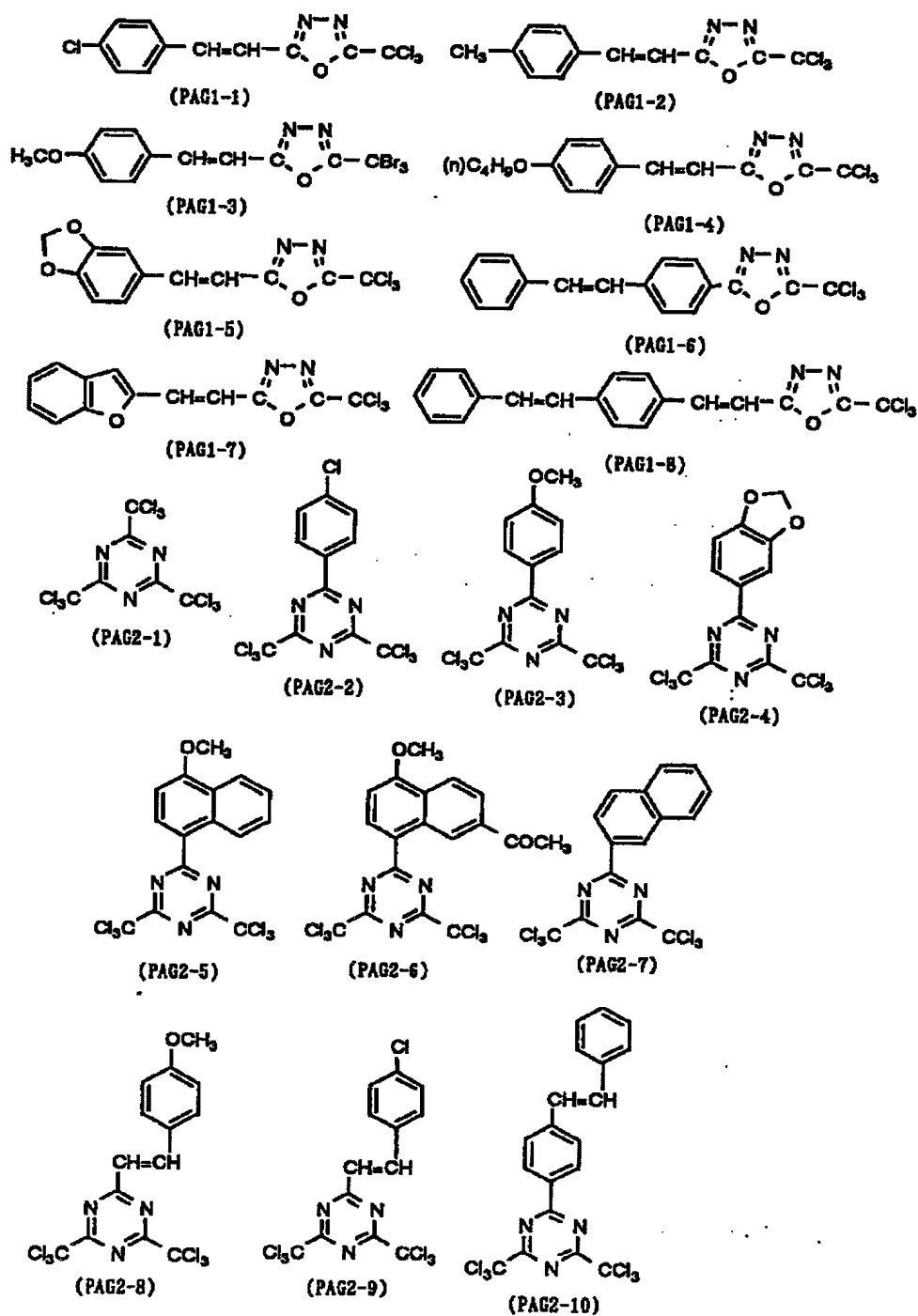
[Formula 34]



[0046] R201 shows among a formula the aryl group which is not permuted [ a permutation or ] and an alkenyl radical, and R202 shows the aryl group which is not permuted [ a permutation or ], an alkenyl radical, an alkyl group, and -C (Y)3. Y shows a chlorine atom or a bromine atom. Although the following compounds can specifically be mentioned, it is not limited to these.

[0047]

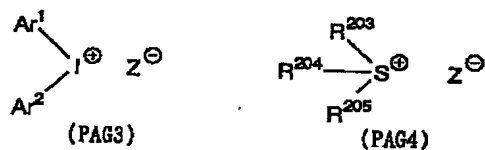
[Formula 35]



[0048] (2) Iodonium salt expressed with the following general formula (PAG3), or sulfonium salt expressed with a general formula (PAG4).

[0049]

[Formula 36]



[0050] Formulas Ar1 and Ar 2 show respectively the aryl group which is not permuted [ a permutation or ] independently here. R203, R204, and R205 show respectively the alkyl group which is not permuted [ a permutation or ] and an aryl group independently.

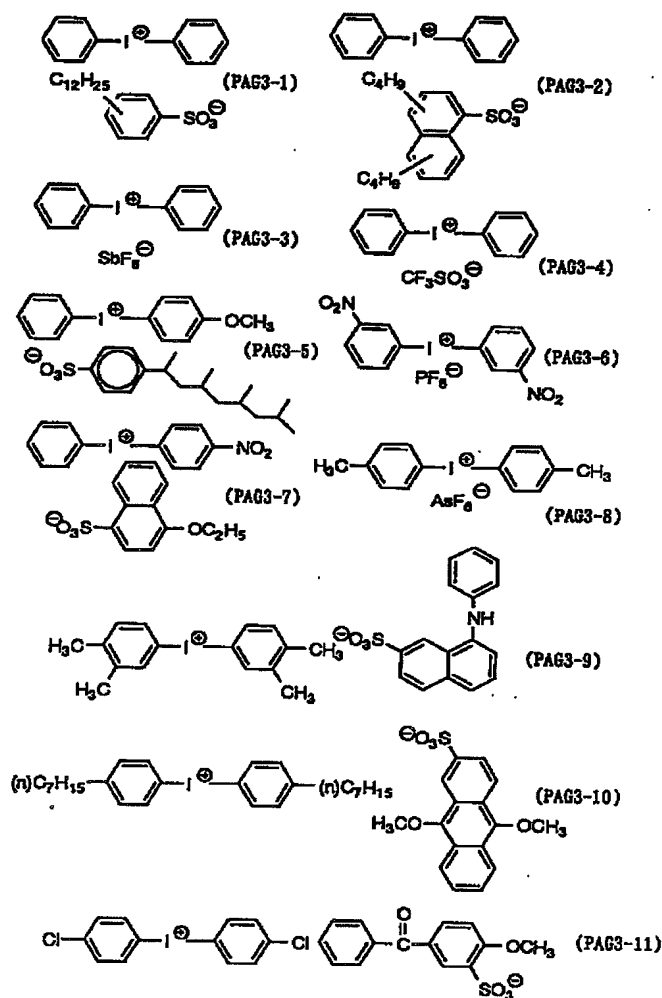
[0051] Z- shows an opposite anion, for example, is condensation polykaryotic aromatic series sulfonic-acid anions, such as perfluoro alkane sulfonic-acid anions, such as  $\text{BF}_4^-$ ,  $\text{AsF}_6^-$ ,  $\text{PF}_6^-$ ,  $\text{SbF}_6^-$ ,  $\text{SiF}_6^{2-}$ ,  $\text{ClO}_4^-$ , and  $\text{CF}_3\text{SO}_3^-$ , a pentafluoro benzenesulfonic acid anion, and a naphthalene-1-sulfonic-acid anion, and an anthraquinone sulfonic acid. Although an anion, a sulfonic group content color, etc. can be mentioned, it is not limited to these.

[0052] Moreover, two, and Ar1 and Ar2 of R203, R204, and R205 may be combined through each single bond or substituent.

[0053] Although the compound shown below as an example is mentioned, it is not limited to these.

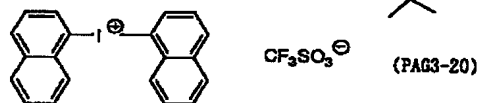
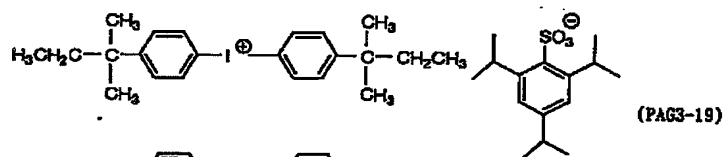
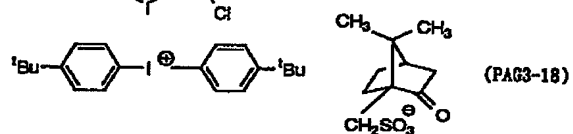
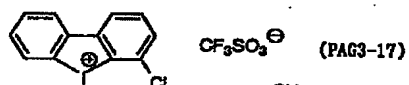
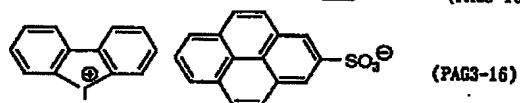
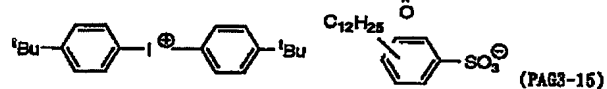
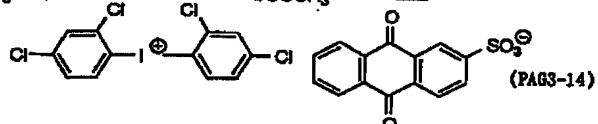
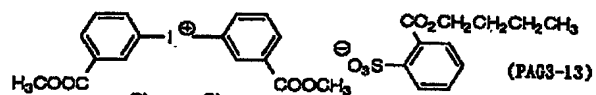
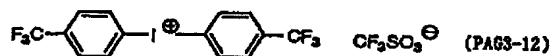
[0054]

[Formula 37]



[0055]

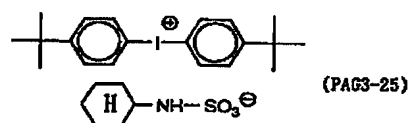
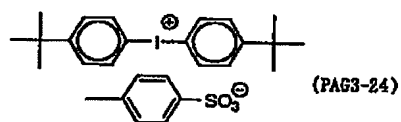
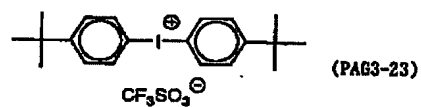
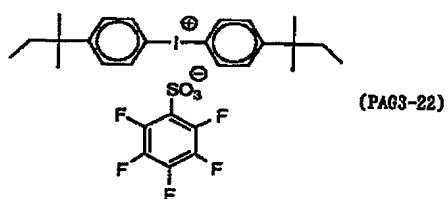
[Formula 38]



[0056]

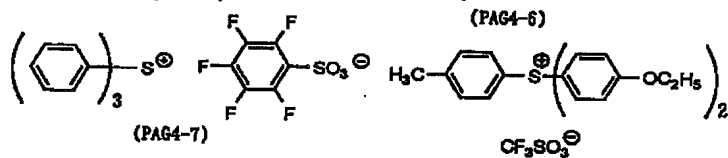
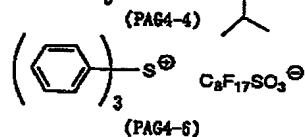
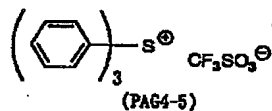
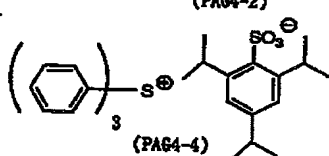
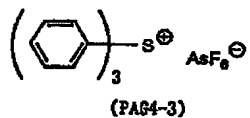
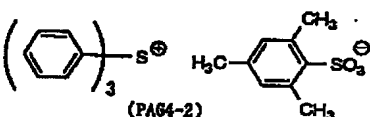
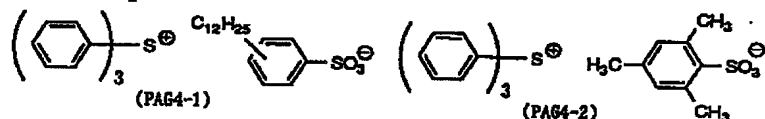
[Formula 39]



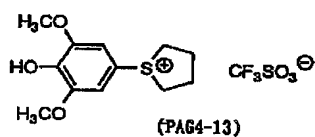
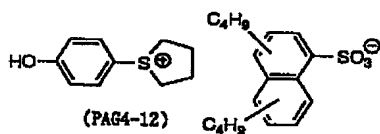
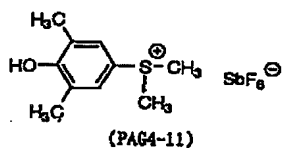
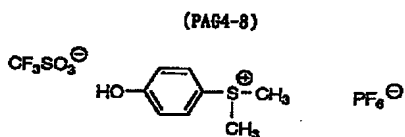
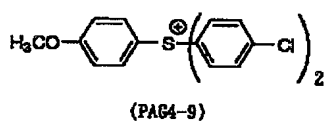


[0057]

[Formula 40]

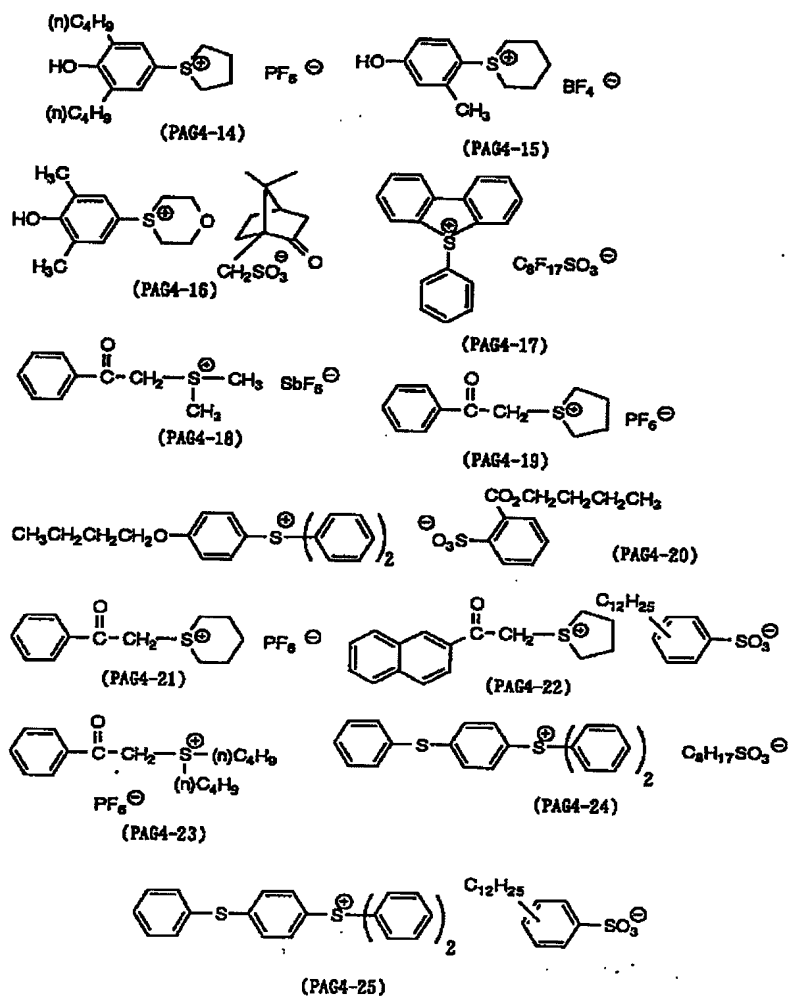


(PAG4-8)



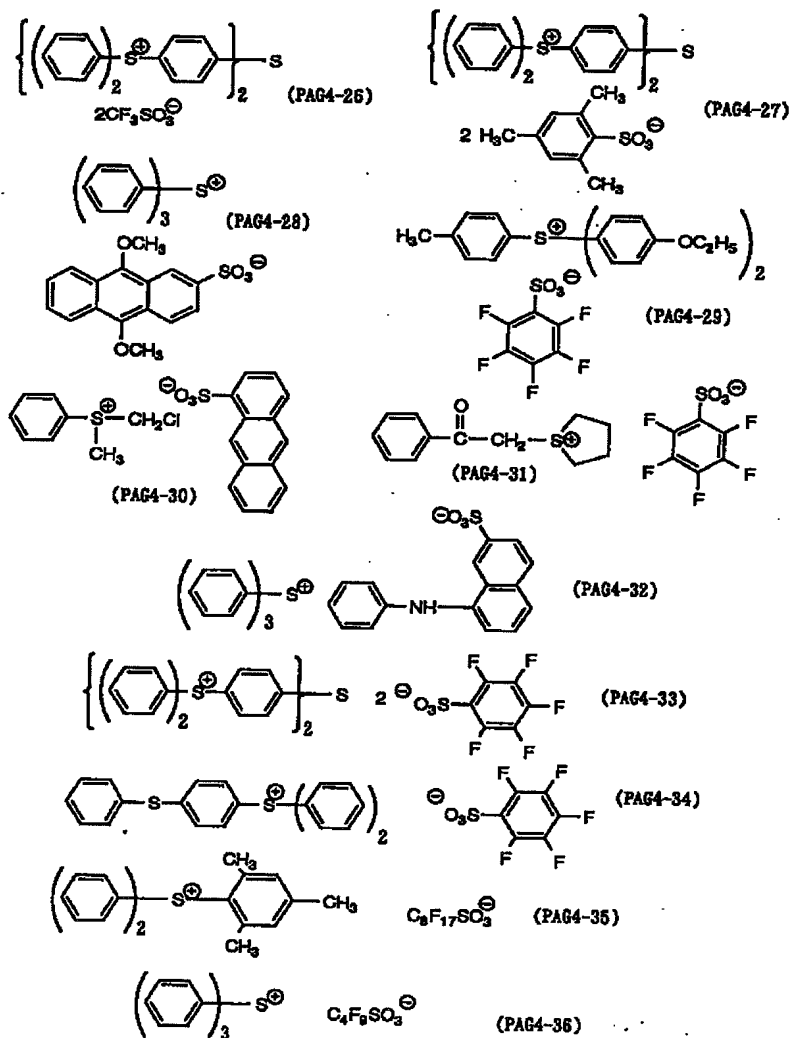
[0058]

[Formula 41]



[0059]

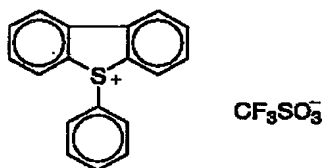
[Formula 42]



[0060]

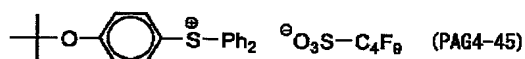
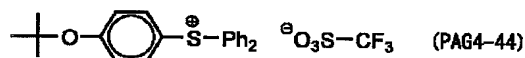
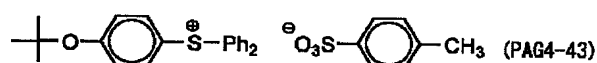
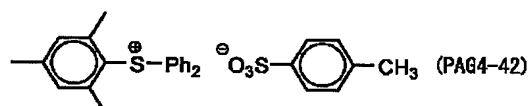
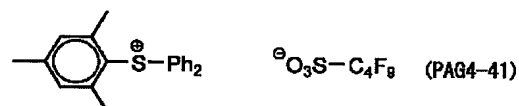
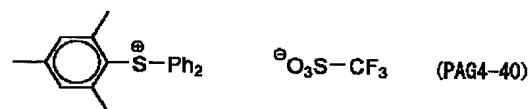
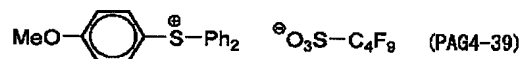
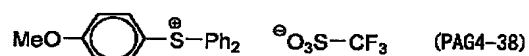
[Formula 43]

PAG4-37



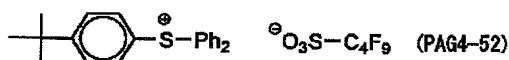
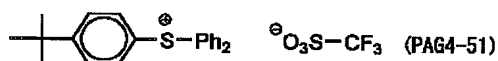
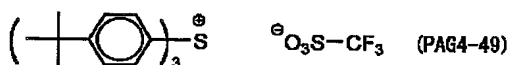
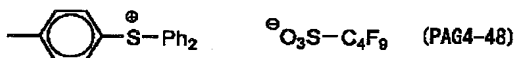
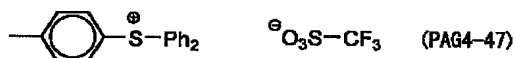
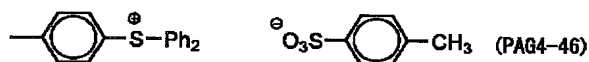
[0061]

[Formula 44]



[0062]

[Formula 45]



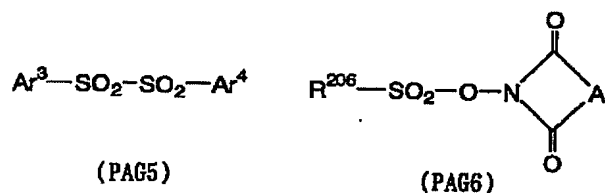
[0063] In the above, Ph expresses a phenyl group. The above-mentioned onium salt shown by the general formula (PAG3) and (PAG4) is well-known, for example, can be compounded by the approach of a publication to U.S. Pat. No. 2,807,648 and said 4,247,473 numbers, JP,53-101,331,A, etc.

[0064] (3) The imino sulfonate derivative expressed with the disulfon derivative or general formula (PAG6)

expressed with the following general formula (PAG5).

[0065]

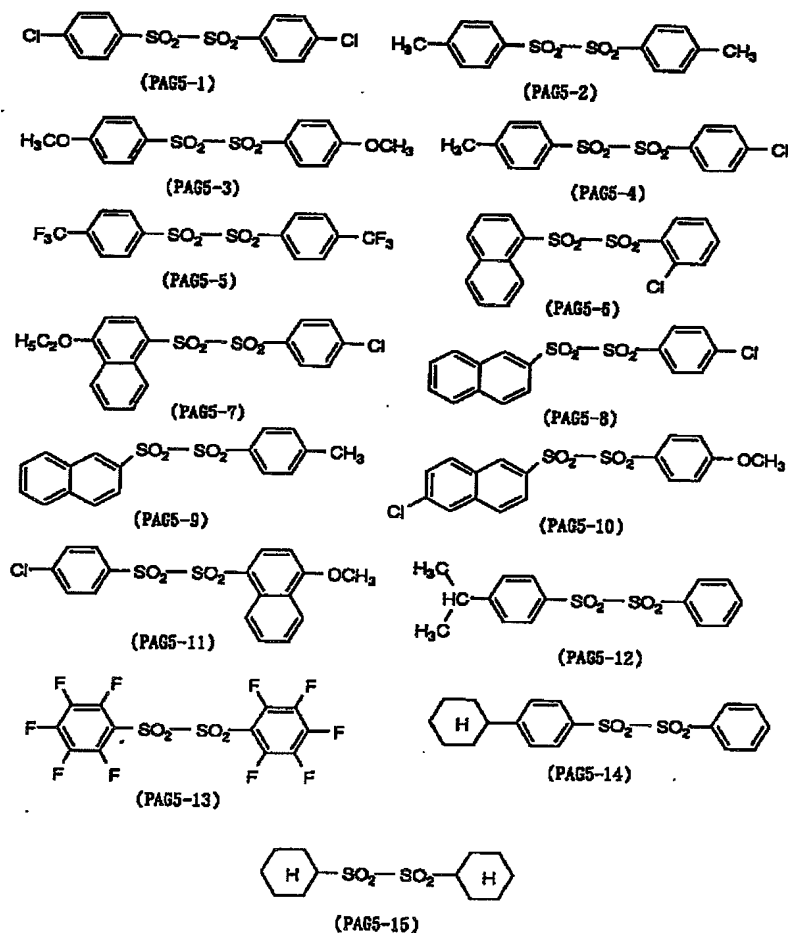
[Formula 46]



[0066] Ar3 and Ar4 show respectively the aryl group which is not permuted [ a permutation or ] independently among a formula. R206 shows the alkyl group which is not permuted [ a permutation or ] and an aryl group. A shows the alkylene group which is not permuted [ a permutation or ], an alkenylene group, and an arylene radical. Although the compound shown below as an example is mentioned, it is not limited to these.

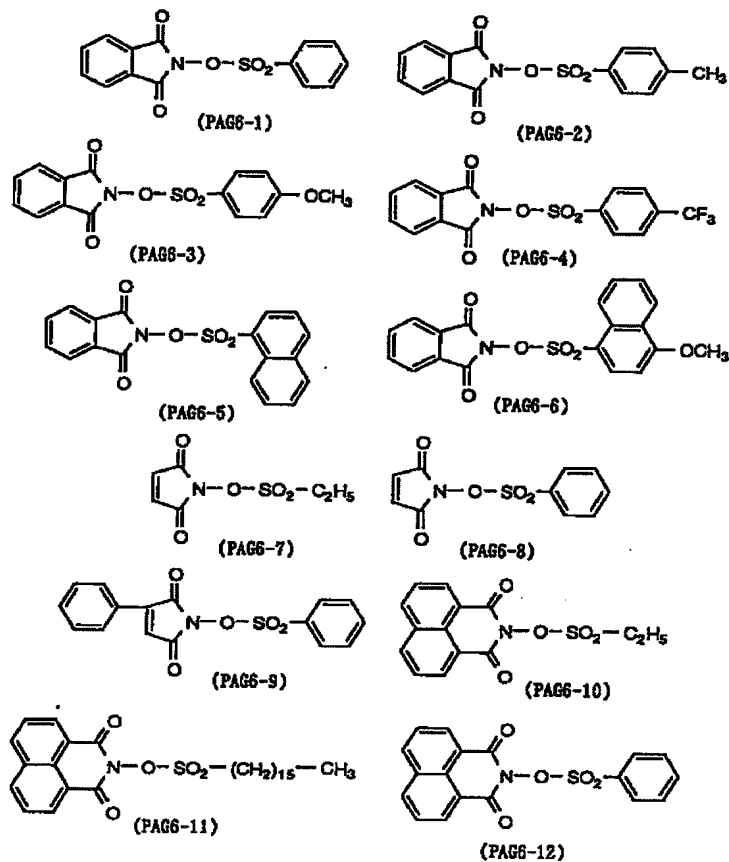
[0067]

[Formula 47]



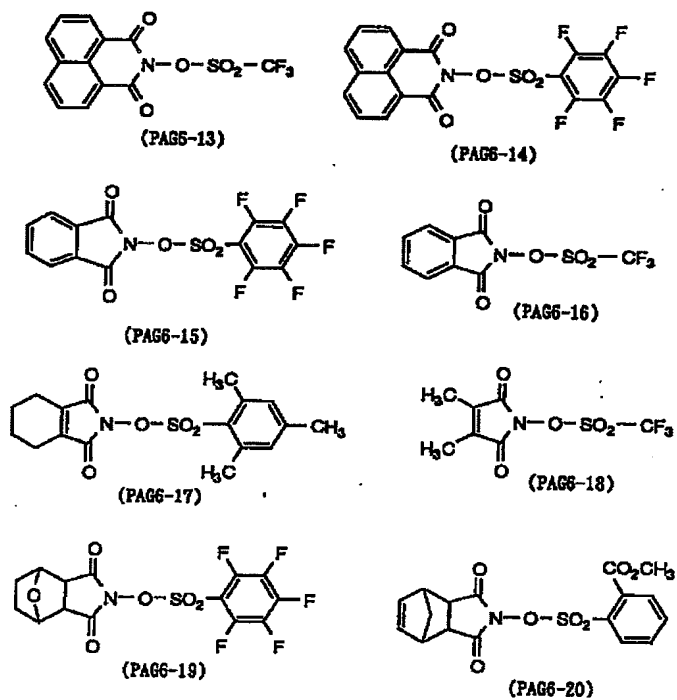
[0068]

[Formula 48]



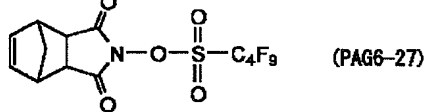
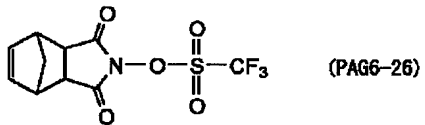
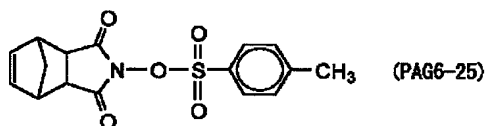
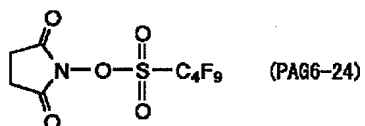
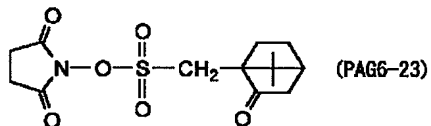
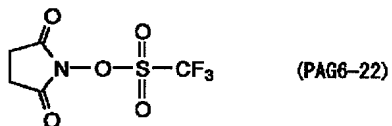
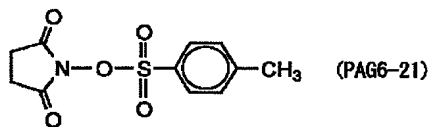
[0069]

[Formula 49]



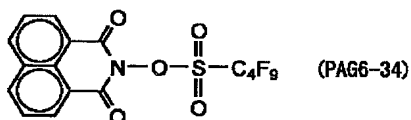
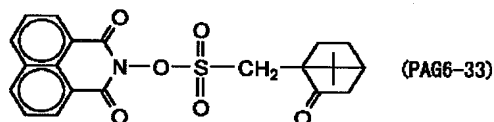
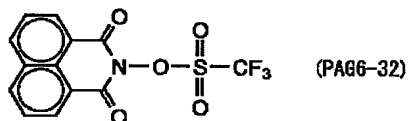
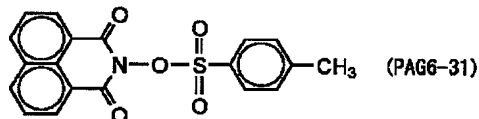
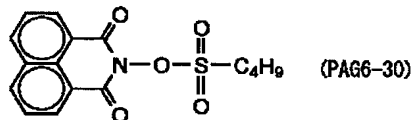
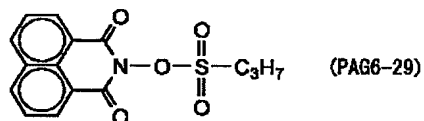
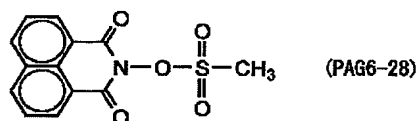
[0070]

## [Formula 50]



[0071]

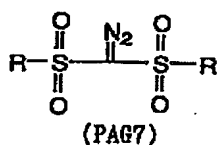
## [Formula 51]



[0072] (4) The diazo disulfon derivative expressed with the following general formula (PAG7).

[0073]

[Formula 52]

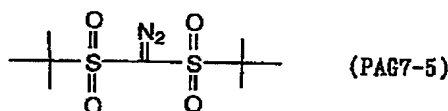
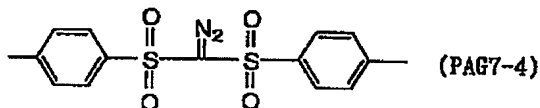
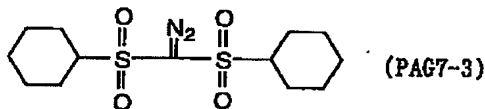
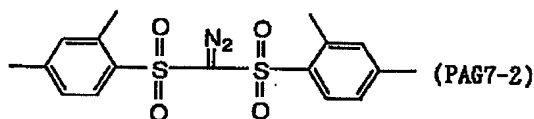
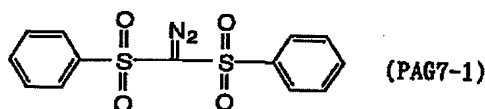


[0074] R expresses a straight chain, branching, an annular alkyl group, or the aryl group that may be permuted here. Although the compound shown below as an example is mentioned, it is not limited to these.

[0075]

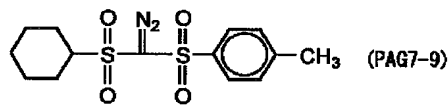
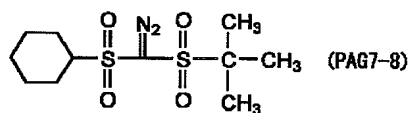
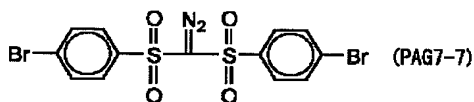
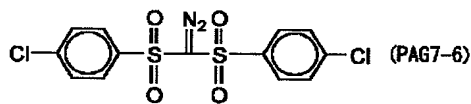
[Formula 53]





[0076]

[Formula 54]



[0077] The addition of a photo-oxide generating agent is usually used in 0.001 – 30% of the weight of the range on the basis of the solid content in a constituent, and is preferably used in 0.5 – 10% of the weight of the range still more preferably 0.3 to 20% of the weight. It becomes [ if there are few additions of a photo-oxide generating agent than 0.001 % of the weight, sensibility will become low, and if there are more additions than 30 % of the weight, the light absorption of a resist will become high too much, and / aggravation of a profile and a process (especially BEKU) margin ] narrow and is not desirable.

[0078] [2] The acidolysis nature resin (it is called for short "the acidolysis nature resin concerning this invention" below) which has the repeat unit expressed with (B) resin, next the (B) above-mentioned general formula (I), the repeat unit expressed with the above-mentioned general formula (II), and the repeat unit expressed with the above-mentioned general formula (III) is explained.

[0079] In the above-mentioned general formula (I), R11-R14 express respectively the radical independently decomposed according to an operation of an acid, a hydrogen atom, a halogen atom, a cyano group, -COOH, -COOR15, -C(=O)-X-A-R16, an alkyl group, or a cyclic-hydrocarbon radical, and at least one of R11-R14 expresses the radical decomposed according to an operation of an acid. Moreover, at least two of R11-R14 may join together, and a ring may be formed. n expresses 0 or 1. Here, R15 expresses an alkyl group, a cyclic-hydrocarbon radical, or the -Y above-mentioned sets. X expresses an oxygen atom, a sulfur atom, -NH-, -NHSO2-, or -NHSO2NH-. A expresses the combination of independent [ which is chosen from the group which consists of single bond, an alkylene group, a cyclo alkylene group, a ether group, a thioether radical, a carbonyl group, and an ester group ], or two radicals or more. R16 expresses -COOH, -COOR15, -CN, a hydroxyl group, an alkoxy group, -CO-NH-R17, -CO-NH-SO2-R17, or the -Y above-mentioned sets. R17 expresses an alkyl group or a cyclic-hydrocarbon radical. In the -Y above-mentioned sets, R21-R30 express a hydrogen atom or an alkyl group independently respectively. a and b express 1 or 2.

[0080] As structure of the radical decomposed according to an operation of an acid, it is -C(=O)-X1-Rp. It is expressed. The inside of a formula, and Rp If it carries out, the 3rd class alkyl groups, such as t-butyl and t-amyl group, An isoboronyl radical, 1-ethoxyethyl radical, a 1-butoxy ethyl group, a 1-iso butoxy ethyl group, 1-alkoxy ethyl groups, such as 1-cyclo hexyloxyethyl radical, 1-methoxymethyl radical, Alkoxy methyl groups, such as a 1-ethoxy methyl group, a 3-oxo-alkyl group, A tetrahydropyranyl group, a tetrahydrofuran radical, a trialkylsilyl ester group, A 3-oxocyclohexyl ester group, a 2-methyl-2-adamantyl radical, mevalonic lactone residue, a 2-(gamma-BOCHIRORAKUTO nil oxy-carbonyl)-2-propyl group, etc. can be mentioned. X1 expresses an oxygen atom, a sulfur atom, -NH-, -NHSO2-, or -NHSO2 NH-.

[0081] As a halogen atom in the above R11-R14, a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc. can be mentioned. As an alkyl group in the above R11-R14, the shape of a straight chain of 1-10 carbon numbers and the letter alkyl group of branching are desirable, are the shape of a straight chain of 1-6 carbon numbers, and a letter alkyl group of branching more preferably, and are a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, and t-butyl still more preferably. As a cyclic-hydrocarbon radical in the above R11-R14, it is an annular alkyl group and owner pons type hydrocarbon, for example, and a cyclo propyl group, a cyclopentyl group, a cyclohexyl radical, an adamantyl radical, a 2-methyl-2-adamantyl radical, a norbornyl radical, a BORONIRU radical, an isoboronyl radical, a tricyclo deca nil radical, a JISHIKURO pentenyl radical, the Novo Renan epoxy group, a menthyl radical, an iso menthyl radical, a neomenthyl radical, a tetracyclo dodecanyl radical, etc. can be mentioned.

[0082] As a ring which at least two of the above R11-R14 combine and form, the ring of the carbon numbers 5-12, such as cyclopentene, a cyclohexene, cycloheptane, and cyclooctane, is mentioned. As an alkoxy group in the above R16, the thing of 1-4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can be mentioned. the alkyl group of each above, the cyclic-hydrocarbon radical, and the alkoxy group may have the substituent further, and can mention a hydroxyl group, a carboxyl group, a cyano group, halogen atoms (for example, a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc.), an alkoxy group, acyl groups (preferably carbon numbers 1-4, for example, a methoxy group, an ethoxy radical, a propoxy group, a butoxy radical, etc.) (for example, a formyl

group, an acetyl group, etc.), acyloxy radicals (for example, acetoxyl radical etc.), etc. as a substituent

[0083] The radical expressed with the following formula can be mentioned as an alkylene group in Above A.

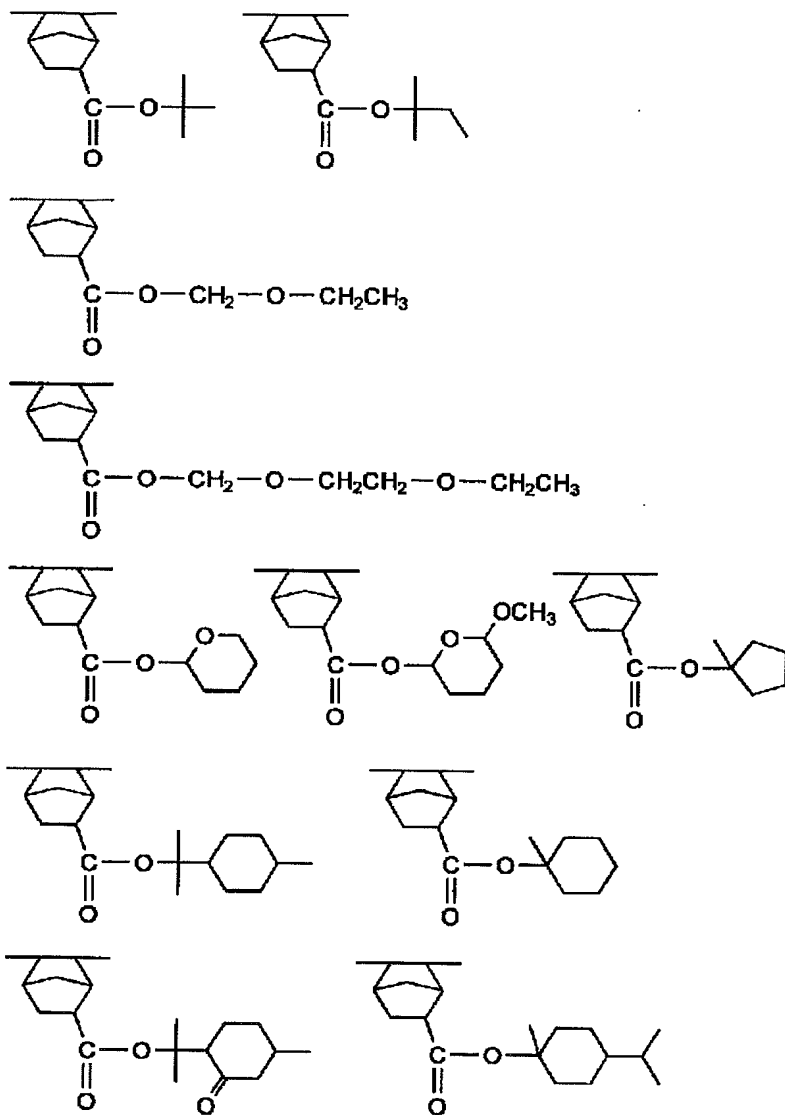
– The inside of a  $[C(Rb)]$  ( $Rc$ )  $r$ -type,  $Rb$ , and  $Rc$  A hydrogen atom, an alkyl group, a permutation alkyl group, a halogen atom, a hydroxyl group, and an alkoxy group are expressed, and even if both are the same, they may differ. As an alkyl group, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, and butyl, are chosen from a methyl group, an ethyl group, a propyl group, and an isopropyl group desirable still more preferably. As a substituent of a permutation alkyl group, a hydroxyl group, a halogen atom, and an alkoxy group (preferably carbon numbers 1–4) can be mentioned. As an alkoxy group, the thing of 1–4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can be mentioned. As a halogen atom, a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc. can be mentioned.  $r$  expresses the integer of 1–10.

[0084] In the  $-Y$  above-mentioned sets,  $R21$ – $R30$  express a hydrogen atom or an alkyl group independently respectively.  $a$  and  $b$  express 1 or 2. As an alkyl group in the above  $R21$ – $R30$ , a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, etc. can be mentioned, for example. The alkyl group as  $R21$ – $R30$  may have the substituent. As this substituent, for example A hydroxyl group, a carboxyl group, a cyano group, A halogen atom (for example, a chlorine atom, a bromine atom, fluorine \*\*\*\*\*, iodine atom), an alkoxy group (desirable — carbon numbers 1–4, for example, a methoxy group, and an ethoxy radical —) Acyl groups, such as a propoxy group and a butoxy radical (carbon number 2–5 preferably) For example, acyloxy radicals, preferably carbon numbers 2–5, for example, an acetoxyl radical, such as a formyl group and an acetyl group, an aryl group, preferably carbon numbers 6–14, for example, a phenyl group, etc. can be mentioned.

[0085] Although the following following are mentioned as an example of the repeat unit expressed with the above-mentioned general formula (I), this invention is not limited to these examples.

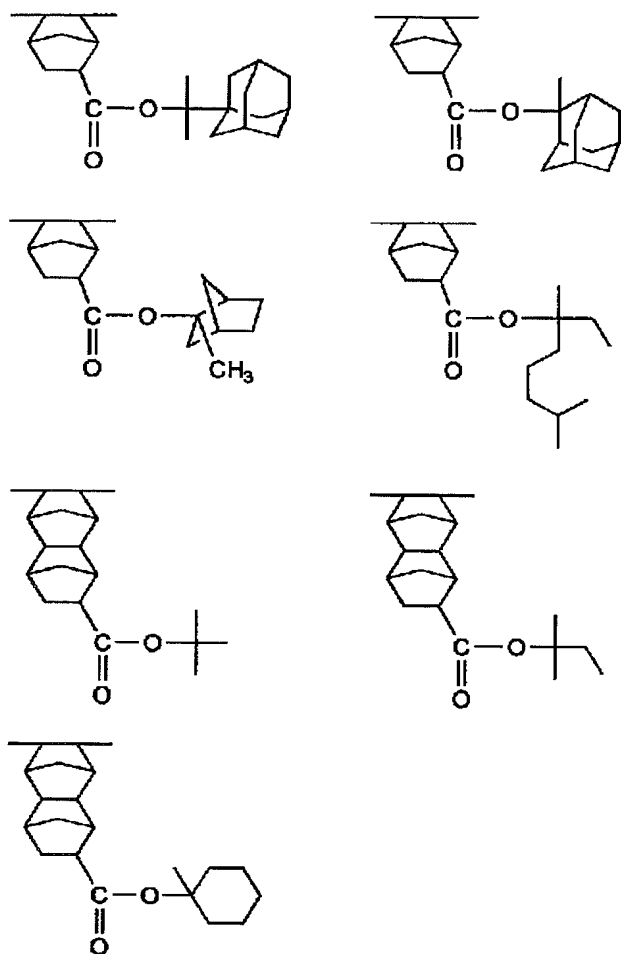
[0086]

[Formula 55]



[0087]

[Formula 56]



[0088] In the above-mentioned general formula (II), Z2 expresses -O- or -N(R41)-. R41 expresses a hydrogen atom, a hydroxyl group, an alkyl group, a halo alkyl group, or -OSO<sub>2</sub>-R42 here. R42 expresses an alkyl group, a halo alkyl group, a cycloalkyl radical, or camphor residue.

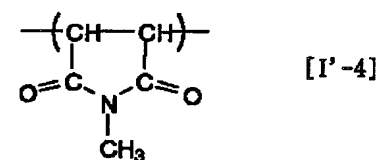
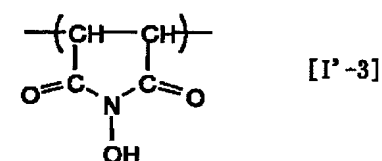
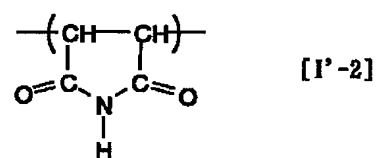
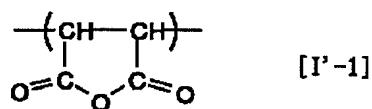
[0089] As an alkyl group in the above R41 and R42, the shape of a straight chain of 1-10 carbon numbers and the letter alkyl group of branching are desirable, are the shape of a straight chain of 1-6 carbon numbers, and a letter alkyl group of branching more preferably, and are a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, and t-butyl still more preferably. Above R41 and R42 As a halo alkyl group which can be set, a trifluoromethyl radical, nano fluoro butyl, a PENTA deca fluoro octyl radical, a TORIKURORO methyl group, etc. can be mentioned. Above R42 As a cycloalkyl radical which can be set, a cyclopentyl group, a cyclohexyl radical, a cyclo octyl radical, etc. can be mentioned.

[0090] The alkyl group as R41 and R42 and a halo alkyl group, the cycloalkyl radical as R42, or camphor residue may have the substituent. As such a substituent, for example A hydroxyl group, a carboxyl group, a cyano group, A halogen atom (for example, a chlorine atom, a bromine atom, fluorine \*\*\*\*\*, iodine atom), an alkoxy group (desirable -- carbon numbers 1-4, for example, a methoxy group, and an ethoxy radical --) Acyl groups, such as a propoxy group and a butoxy radical (carbon number 2-5 preferably) For example, acyloxy radicals, preferably carbon numbers 2-5, for example, an acetoxy radical, such as a formyl group and an acetyl group, an aryl group, preferably carbon numbers 6-14, for example, a phenyl group, etc. can be mentioned.

[0091] Although following [I'-1] - [I'-7] is mentioned as an example of the repeat unit expressed with the above-mentioned general formula (II), this invention is not limited to these examples.

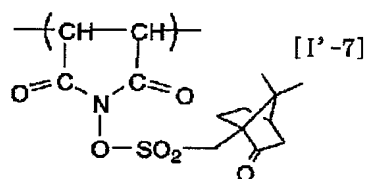
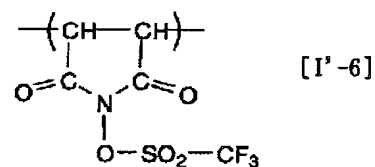
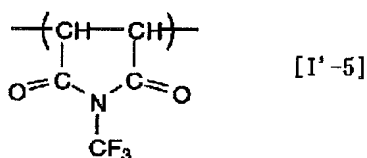
[0092]

[Formula 57]



[0093]

[Formula 58]



[0094] Next, the repeat unit expressed with a general formula (III) is explained. In a formula (III), R91 expresses a hydrogen atom, low-grade alkyl group, and halogen atom or a cyano group. As a low-grade alkyl

group of R91, the thing of carbon numbers 1–5 is desirable, and a methyl group, an ethyl group, a propyl group, butyl, a pentyl radical, etc. are mentioned. This low-grade alkyl group may have the substituent further. As such a substituent, for example a hydroxyl group, a carboxyl group, a cyano group, a halogen atom (for example, a chlorine atom, a bromine atom, fluorine \*\*\*\*\*, iodine atom), an alkoxy group (desirable — carbon numbers 1–4, for example, a methoxy group, and an ethoxy radical —) Acyl groups, such as a propoxy group and a butoxy radical (carbon number 2–5 preferably) For example, acyloxy radicals, preferably carbon numbers 2–5, for example, an acetoxy radical, such as a formyl group and an acetyl group, an aryl group, preferably carbon numbers 6–14, for example, a phenyl group, etc. can be mentioned.

[0095] X5 expresses  $-O-$ ,  $-S-$ ,  $-NR_{93}-$ , or  $-NR_{93}SO_2-$ . R93 expresses a hydrogen atom, the shape of a chain, and an annular alkyl group. As a chain-like alkyl group as R93, it is a low-grade alkyl group, and the thing of carbon numbers 1–5 is desirable, and a methyl group, an ethyl group, a propyl group, butyl, a pentyl radical, etc. are mentioned. As an annular alkyl group, the thing of carbon numbers 3–12 is mentioned, for example. These may have the substituent further. As a substituent For example, a hydroxyl group, a carboxyl group, a cyano group, a halogen atom for example, (a chlorine atom, a bromine atom, fluorine \*\*\*\*\* and iodine atom), and an alkoxy group (desirable — carbon numbers 1–4, for example, a methoxy group, —) Acyl groups, such as an ethoxy radical, a propoxy group, and a butoxy radical (carbon number 2–5 preferably) For example, acyloxy radicals, preferably carbon numbers 2–5, for example, an acetoxy radical, such as a formyl group and an acetyl group, an aryl group, preferably carbon numbers 6–14, for example, a phenyl group, etc. can be mentioned.

[0096] B expresses single bond or a connection radical. The combination of independent [ which is chosen from the group which consists of an alkylene group, a cyclo alkylene group, an ether group, a thioether radical, a carbonyl group, and an ester group, for example as a connection radical of B ], or two radicals or more can be mentioned. As a cyclo alkylene group of B, the thing of carbon numbers 3–10 is mentioned preferably, for example, a cyclo pentene radical, a cyclo hexylene radical, and a cyclo octylene radical can be mentioned. The radical expressed with the following type can be mentioned as an alkylene group of B.

– Reach  $[C(RX)](RY)Z-R_x$  and  $R_y$  expresses respectively the shape of a chain which may have the hydrogen atom, the hydroxyl group, the halogen atom, and the substituent, an annular alkyl group, an alkoxy group, an alkenyl radical, an aryl group, or an aralkyl radical independently. However, it may join together mutually and  $R_x$  and  $R_y$  may form an annular alkyl ring. As a chain-like alkyl group of  $R_x$  or  $R_y$ , the alkyl group of the shape of a straight chain and the letter of branching is mentioned, and you may have the substituent. As an alkyl group of the shape of a straight chain, and the letter of branching, the shape of a straight chain of 1–12 carbon numbers and the letter alkyl group of branching are desirable, are the shape of a straight chain of 1–10 carbon numbers, and a letter alkyl group of branching more preferably, and are a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, a pentyl radical, a neopentyl radical, a hexyl group, a heptyl radical, an octyl radical, a nonyl radical, and a decyl group still more preferably As an annular alkyl group, the thing of 3–30 carbon numbers is mentioned, and hetero atoms, such as an oxygen atom and a nitrogen atom, may be included. Specifically, a cyclo propyl group, a cyclopentyl group, a cyclohexyl radical, an adamantyl radical, a norbornyl radical, a BORONIRU radical, a tricyclo deca nil radical, a JISHIKURO pentenyl radical, the Novo Renan epoxy group, a menthyl radical, an iso menthyl radical, a neomenthyl radical, a tetracyclo dodecanyl radical, steroid residue, a tetrahydropyranyl group, a

morpholino radical, etc. can be mentioned. As an alkoxy group, generally, 1–4 things are mentioned still more preferably, for example, a methoxy group, an ethoxy radical, a propoxy group, a butoxy radical, etc. can be mentioned 1–10 carbon numbers preferably 1–12 carbon numbers. As an alkenyl radical, the alkenyl radical of 2–6 carbon numbers is mentioned, and you may have the substituent. Specifically, a vinyl group, a propenyl radical, an allyl group, a butenyl group, a pentenyl radical, a hexenyl radical, a cyclopentenyl radical, a cyclohexenyl group, a 3-oxo-cyclohexenyl group, a 3-oxo-cyclopentenyl radical, a 3-oxo-indenyl group, etc. are mentioned. The annular alkenyl radical may contain the oxygen atom among these. As an aryl group, the thing of 6–10 carbon numbers is mentioned, and you may have the substituent. Specifically, a phenyl group, a tolyl group, a naphthyl group, etc. are mentioned. As an aralkyl radical, benzyl, a phenethyl radical, a naphthyl methyl group, a naphthyl ethyl group, and a mesityl methyl group can be mentioned. As a substituent which the above-mentioned shape of a chain, an annular alkyl group, the alkoxy group, the alkenyl radical, the aryl group, or the aralkyl radical may have for example, a carboxyl group, a cyano group, a hydroxyl group, and a halogen atom (a chlorine atom —) alkoxy groups (desirable — carbon numbers 1–4, for example, a methoxy group, —), such as a bromine atom, a fluorine atom, and iodine atom. An ethoxy radical, a propoxy group, a butoxy radical, an acetyl amide group, an alkoxy carbonyl group, An acyl group (preferably carbon numbers 2–10, for example, a formyl group, an acetyl group, a propionyl radical), an acyloxy radical, preferably carbon numbers 2–10, for example, an acetoxyl radical, and an aryl group, preferably carbon numbers 6–14, for example, a phenyl group, are mentioned. About the aryl group or the aralkyl radical, you may have alkyl groups (preferably carbon numbers 1–5, for example, a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, a cyclopropyl group, cyclobutyl, a cyclopentyl group, etc.) further as a substituent as Rx or Ry. The alkyl group as this substituent may have substituents, such as a hydroxyl group, a halogen atom, and an alkoxy group (preferably carbon numbers 1–4, for example, a methoxy group, an ethoxy radical, a propoxy group, a butoxy radical), further. Z is the integer of 1–10 and is 1–4 preferably.

[0097] R92 expresses the radical expressed with either a hydrogen atom, the shape of a chain, an annular alkyl group, an alkoxy group, a hydroxyl group, a carboxy group, a cyano group, —COOR<sub>94</sub> or above-mentioned general formula (IV)–(X). as the chain-like alkyl group as R92 and R94 — general — carbon numbers 1–30 — the thing of 6–20 is mentioned preferably. For example, a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, a pentyl radical, a neopentyl radical, a hexyl group, a heptyl radical, an octyl radical, a nonyl radical, a decyl group, an undecyl radical, the dodecyl, a tridecyl radical, a tetradecyl radical, a pentadecyl group, a hexadecyl radical, a heptadecyl radical, an octadecyl radical, a nonadecyl group, a ray KOSHIRU radical, etc. can be mentioned. as the annular alkyl group as R92 and R94 — general — carbon numbers 3–40 — the thing of 6–20 is mentioned preferably. For example, a cyclopropyl group, a cyclopentyl group, a cyclohexyl radical, an adamantyl radical, a norbornyl radical, a BORONIRU radical, a tricyclo decanil radical, a JISHIKURO pentenyl radical, the Novo Renan epoxy group, a menthyl radical, an isomenthyl radical, a neomenthyl radical, a tetracyclo dodecanyl radical, steroid residue, a tetrahydropyranyl group, a morpholino radical, etc. can be mentioned.

[0098] The chain-like alkyl group as R92 and R94 may have the substituent. As a substituent, for example A hydroxyl group, a carboxyl group, a cyano group, a halogen atom for example, (a chlorine atom, a bromine atom, fluorine \*\*\*\*\* and iodine atom), and an alkoxy group (desirable — carbon numbers 1–4, for example, a methoxy group, —) Alkoxy carbonyl groups, such as an ethoxy radical, a propoxy group, and a butoxy

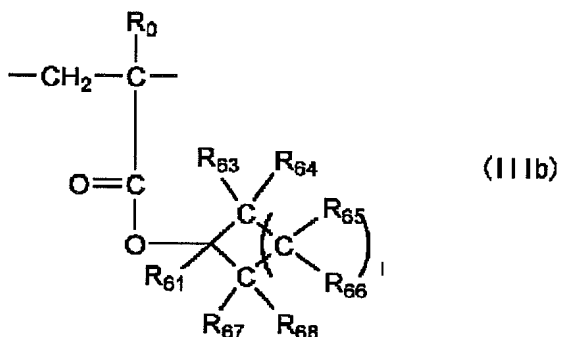
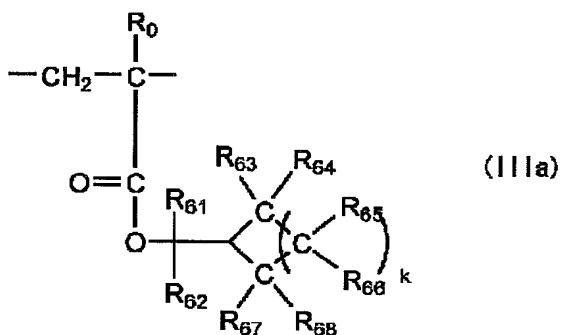


radical, Acyl groups (preferably carbon numbers 2–5, for example, a formyl group, an acetyl group, etc.), an acyloxy radical, preferably carbon numbers 2–5, for example, an acetoxy radical, an aryl group, preferably carbon numbers 6–14, for example, a phenyl group, an acetyl amide group, etc. can be mentioned. As an alkoxy group in an alkoxy carbonyl group, the thing of 1–4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can be mentioned here, for example. The annular alkyl group as R92 and R94 as a substituent -- a carboxyl group, a cyano group, and a halogen atom (a chlorine atom --) a bromine atom, fluorine \*\*\*\*\*, iodine atom, and an alkoxy group (desirable -- carbon numbers 1–4, for example, a methoxy group, --) Alkoxy carbonyl groups, such as an ethoxy radical, a propoxy group, and a butoxy radical, You may have acyl groups (preferably carbon numbers 2–5, for example, a formyl group, an acetyl group, etc.), the acyloxy radical, preferably carbon numbers 2–5, for example, an acetoxy radical, the aryl group, preferably carbon numbers 6–14, for example, a phenyl group, and the acetyl amide group. As an alkoxy group in an alkoxy carbonyl group, the thing of 1–4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can be mentioned here, for example.

[0099] The repeat unit expressed with a following general formula (IIIa) or the following above-mentioned general formula (IIIb) as a repeat unit expressed with the above-mentioned general formula (III) whose R92 is an annular alkyl group is desirable.

[0100]

[Formula 59]



[0101] R0 expresses a hydrogen atom, low-grade alkyl group, and halogen atom and a cyano group among a general formula (IIIa) and a general formula (IIIb). R61 and R62 express a low-grade alkyl group. R63–R68 express a hydrogen atom, a low-grade alkyl group, a lower alkoxy group, or a halogen atom independently respectively. R63, R64, or R65 and R66 may become together, and they may form a carbonyl group. R63 and R65 may connect and may form an alkylene chain. k and l are the integers of 2–5.

[0102] In the above-mentioned general formula (IIIa) and (IIIb) the repeat unit expressed, existence of the 3rd class carbon atom which R61 has combined shows acidolysis nature. R0 is a hydrogen atom preferably. The low-grade alkyl groups as R0, R61-R68 are carbon numbers 1-6, and are carbon numbers 1-4 preferably. As an example, a methyl group, an ethyl group, a straight chain or a branching propyl group, a straight chain, or branching butyl can be mentioned. The lower alkoxy groups as R63-R68 are carbon numbers 1-6, and are carbon numbers 1-4 preferably. As an example, a methoxy group, an ethoxy radical, a straight chain or a branching propoxy group, a straight chain, or a branching butoxy radical can be mentioned. The low-grade alkyl group as R0, R61-R68 and the lower alkoxy group as R63-R68 may have the substituent. As a substituent, alkoxy groups (preferably carbon numbers 1-3), such as halogen atoms, such as a chlorine atom and a bromine atom, a methoxy group, and an ethoxy radical, etc. can be mentioned, for example.

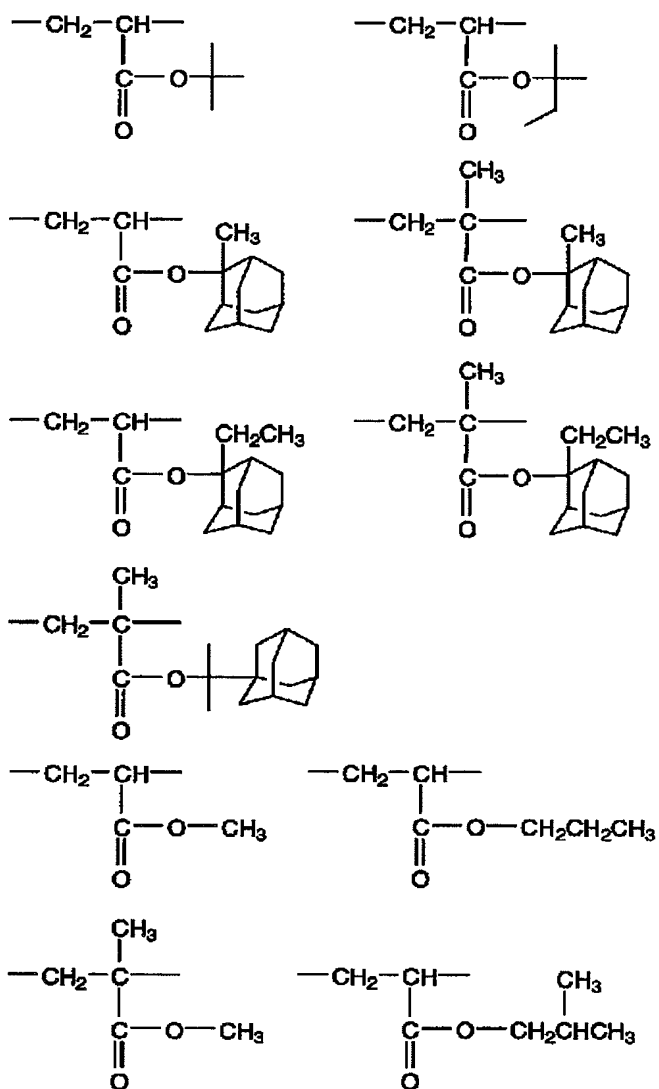
[0103] R63, R64, or R65 and R66 may become together, and they may form a carbonyl group. k and l -- desirable -- 2-4 -- it is 2 or 3 still more preferably. As an alkylene chain which R63 and R65 may connect and form, a methylene chain, an ethylene chain, a propylene chain, etc. are three or less carbon numbers preferably.

[0104] as the alkoxy group of R92 -- general -- carbon numbers 1-30 -- desirable -- 3-20 -- it is the thing of 4-15 still more preferably, for example, a methoxy group, an ethoxy radical, a propoxy group, a butoxy radical, etc. can be mentioned. The alkoxy group of R92 may have the substituent further, and is the same as that of what was explained as a substituent to the shape of a chain and annular alkyl group as R92, for example as a substituent.

[0105] Although R92 gives hereafter the example of the repeat unit expressed with an alkyl group, an alkoxy group, the repeat unit expressed with the general formula (III) which is a hydrogen atom, a general formula (IIIa), and a general formula (IIIb), it is not limited to these.

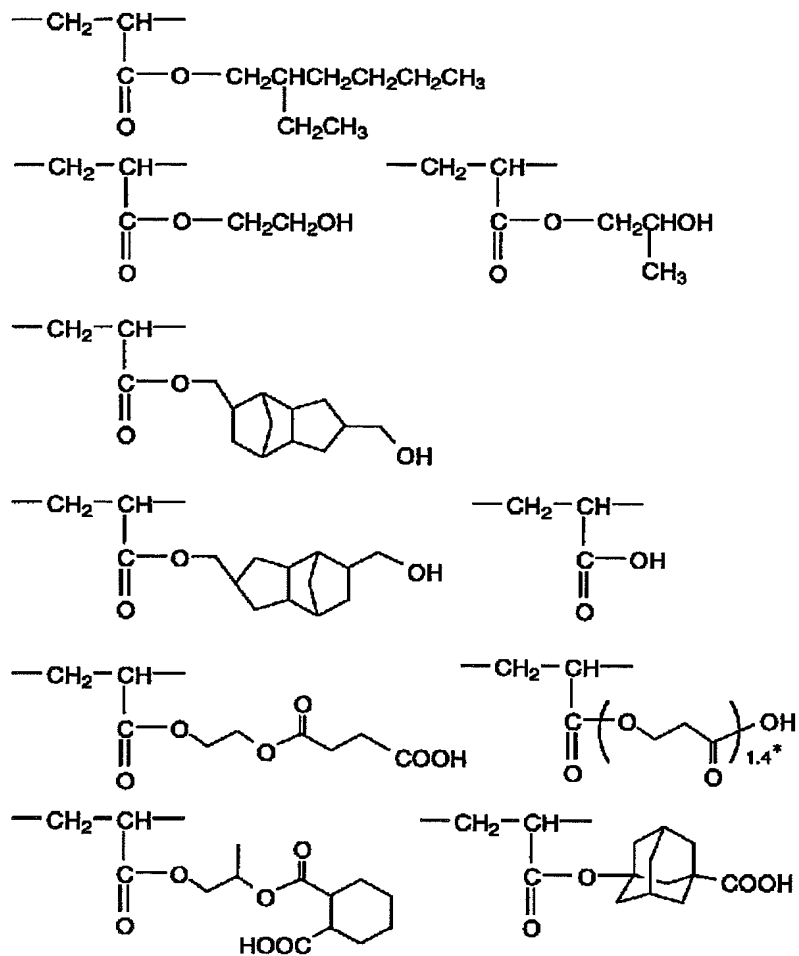
[0106]

[Formula 60]



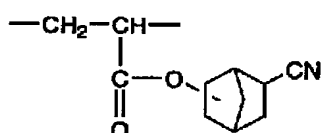
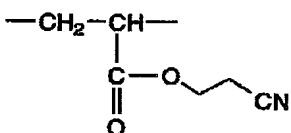
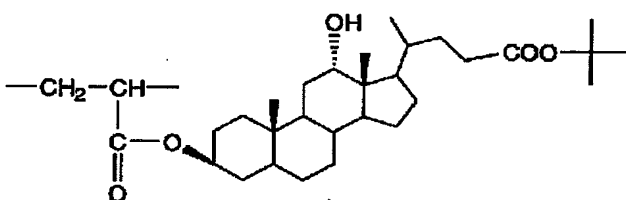
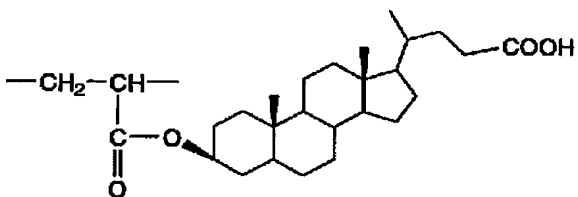
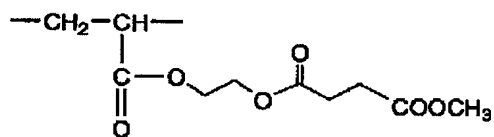
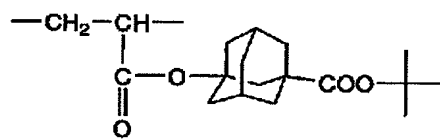
[0107]

[Formula 61]



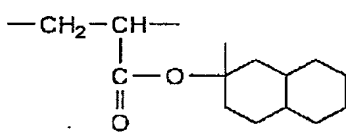
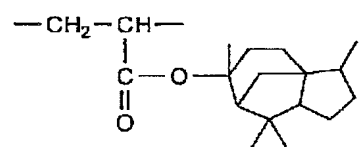
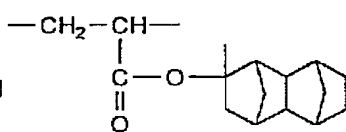
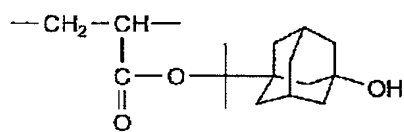
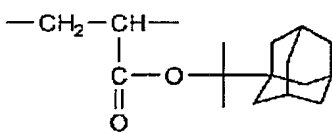
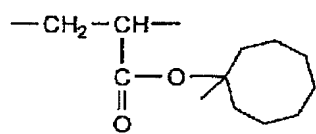
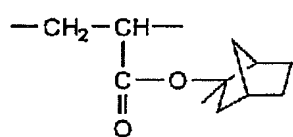
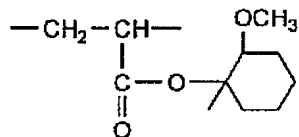
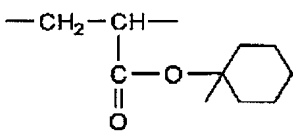
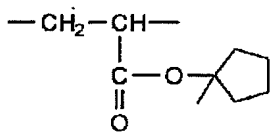
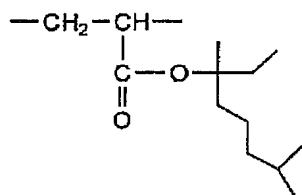
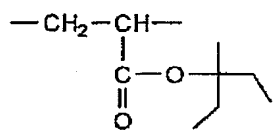
[0108]

[Formula 62]



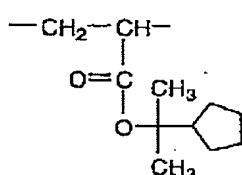
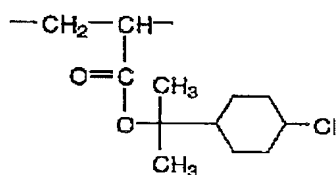
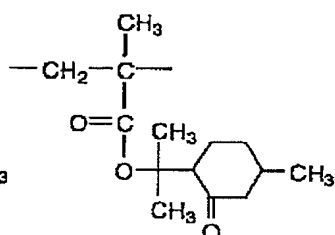
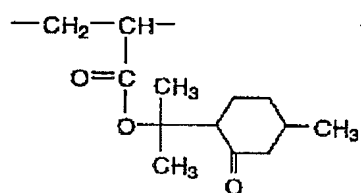
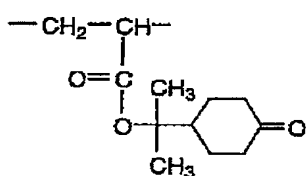
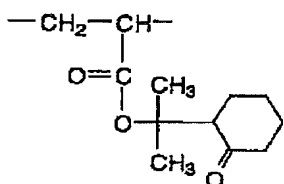
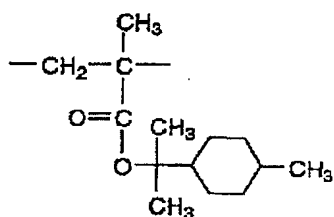
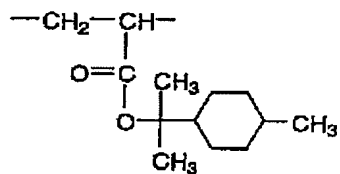
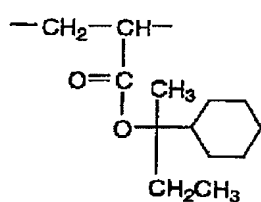
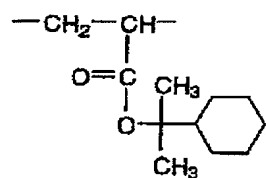
[0109]

[Formula 63]



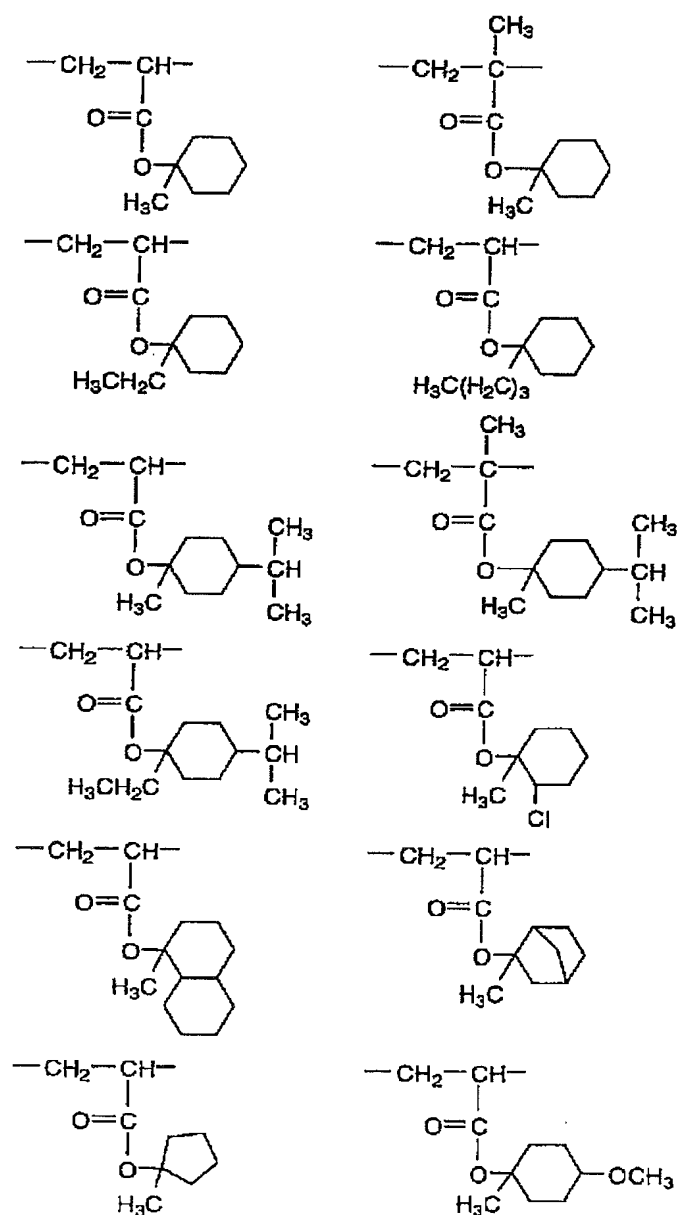
[0110]

[Formula 64]



[0111]

[Formula 65]

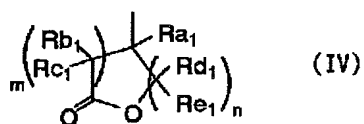


[0112] \*) -- it is mixing of the unit from which the number of the radicals in a parenthesis differs, and mean having 1.4 radicals in a parenthesis on an average.

[0113] Furthermore, R92 in a formula (III) explains the repeat structural unit which is the structure expressed with the following general formula (IV).

[0114]

[Formula 66]



[0115] Ra1, Rb1, Rc1, Rd1, and Re1 express a hydrogen atom or the alkyl group of carbon numbers 1-4 independently respectively. m and n express the integer of 0-3 independently respectively, and m+n is six or

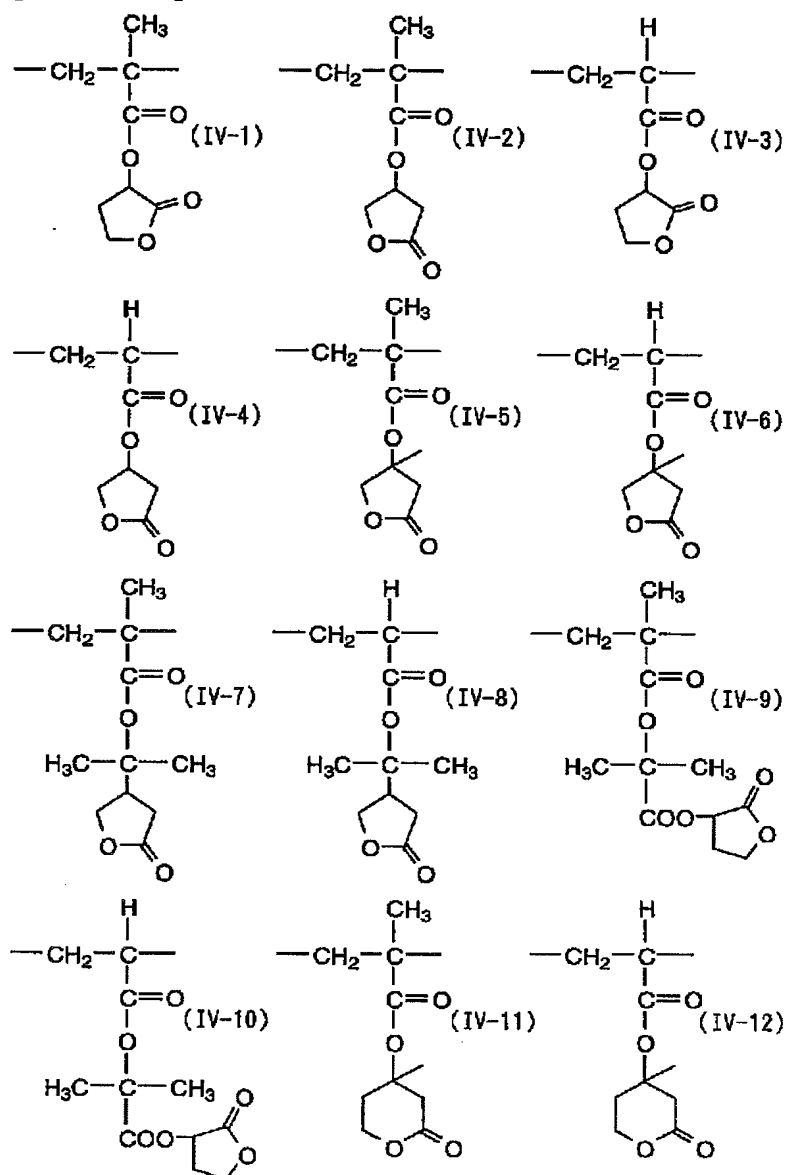


less [ 2 or more ]. As an alkyl group of the carbon numbers 1-4 of Ra1-Re1, a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, t-butyl, etc. can be mentioned. These alkyl groups may be permuted by substituents, such as an alkoxy group (preferably carbon numbers 1-4).

[0116] Although the example of a repeat structural unit of having the structure of a general formula (IV) is shown hereafter, it is not limited to these.

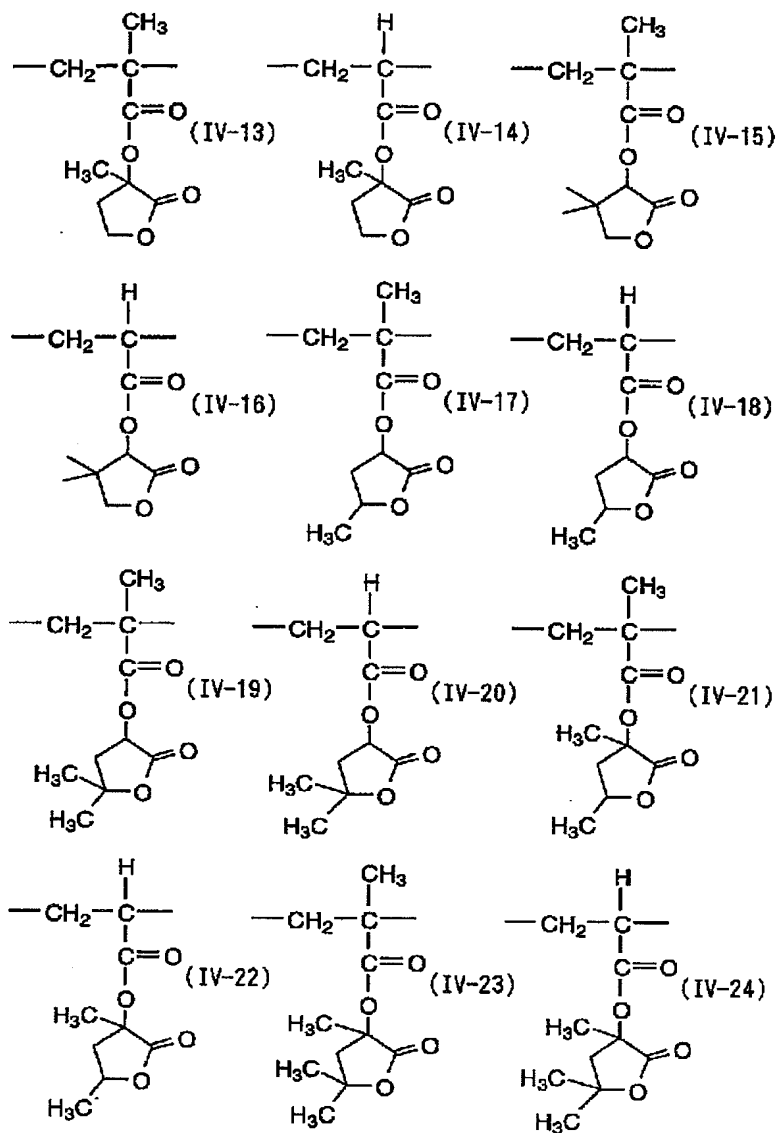
[0117]

[Formula 67]



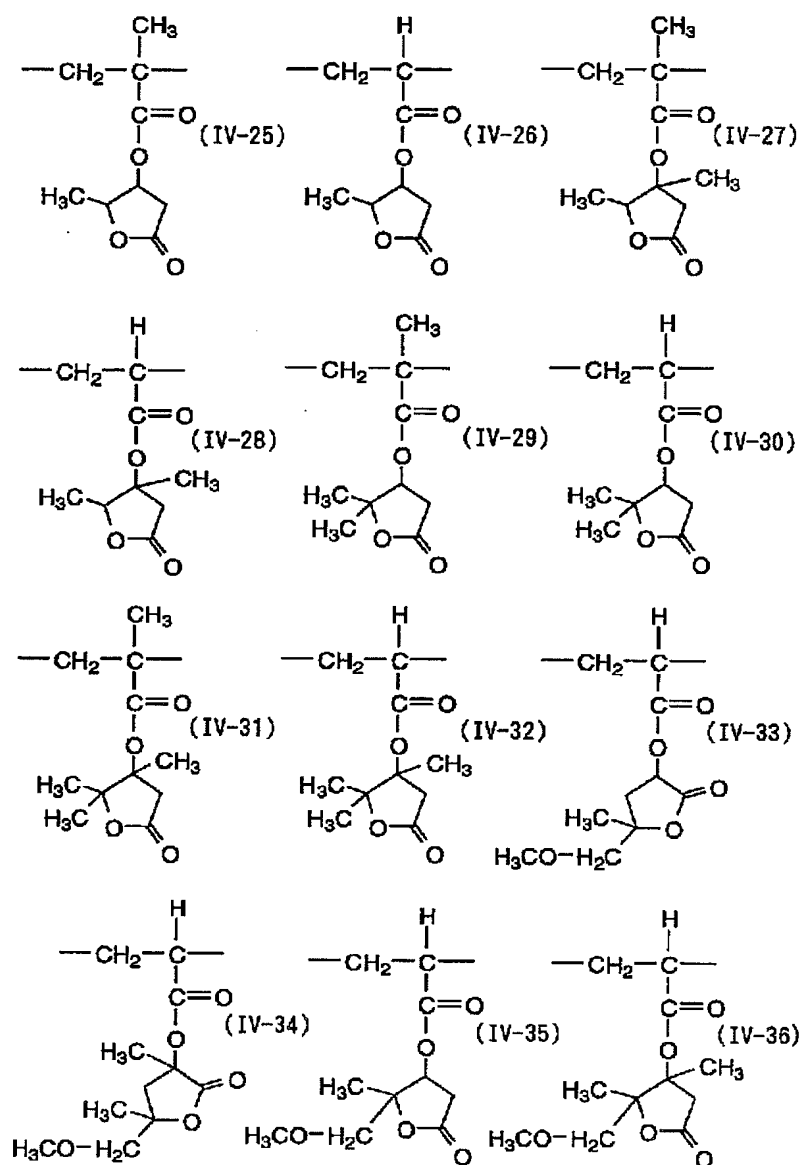
[0118]

[Formula 68]



[0119]

[Formula 69]

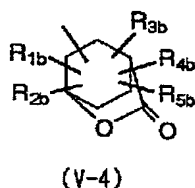
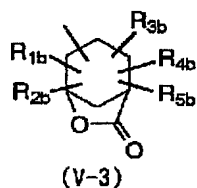
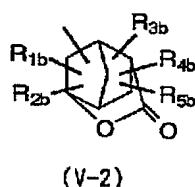
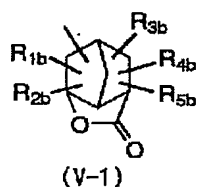


[0120] In the example of a repeat unit of having the structure of the above-mentioned general formula (IV), — (IV-36) is desirable from the point that an exposure margin becomes fitness more (IV-17). Furthermore, what has acrylate structure from the point that edge roughness becomes good, as structure of a general formula (IV) is desirable.

[0121] The repeat unit structure of having the radical expressed with the further following general formula (V-1) – (V-4) either is explained.

[0122]

[Formula 70]



[0123] In general formula (V-1) – (V-4), R1 b–R5b expresses a hydrogen atom, an alkyl group, a cycloalkyl radical, or an alkenyl radical independently respectively. Two of R1 b–R5b may form a ring unitedly.

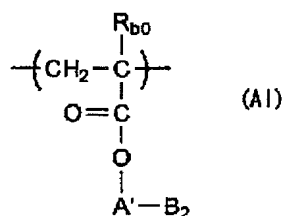
[0124] In general formula (V-1) – (V-4), the alkyl group of the shape of a straight chain and the letter of branching is mentioned as an alkyl group in R1 b–R5b. As an alkyl group of the shape of a straight chain, and the letter of branching, the shape of a straight chain of 1–12 carbon numbers and the letter alkyl group of branching are desirable, are the shape of a straight chain of 1–10 carbon numbers, and a letter alkyl group of branching more preferably, and are a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, t-butyl, a pentyl radical, a hexyl group, a heptyl radical, an octyl radical, a nonyl radical, a decyl group still more preferably. As a cycloalkyl radical in R1 b–R5b, the thing of 3–8 carbon numbers, such as a cyclo propyl group, a cyclopentyl group, a cyclohexyl radical, a cycloheptyl radical, and a cyclo octyl radical, is desirable. As an alkenyl radical in R1 b–R5b, the thing of 2–6 carbon numbers, such as a vinyl group, a propenyl radical, a butenyl group, and a hexenyl radical, is desirable, for example. Moreover, as a ring which two of R1 b–R5b combine and form, three to 8 membered-rings, such as a cyclopropane ring, a cyclobutane ring, a cyclopentane ring, a cyclohexane ring, and a cyclooctane ring, are mentioned.

[0125] Moreover, the ring which two of the alkyl group as R1b–R5b, a cycloalkyl radical, an alkenyl radical, and R1 b–R5b combine and form may have the substituent, respectively. As a desirable substituent, a hydroxyl group, a carboxy group, a nitro group, a cyano group, a halogen atom (a fluorine atom, a chlorine atom, a bromine atom, iodine atom), the alkoxy group of 1–4 carbon numbers, the alkoxy carbonyl group of 2–5 carbon numbers, the acyl group of 2–5 carbon numbers, the acyloxy radical of 2–5 carbon numbers, etc. can be mentioned. In addition, R1 b–R5b in general formula (V-1) – (V-4) may be connected with any of the carbon atom which constitutes the annular frame.

[0126] As what that has the radical expressed with general formula (V-1) – (V-4) and is desirable as a repeat unit, the repeat unit expressed with the following general formula (AI) is mentioned.

[0127]

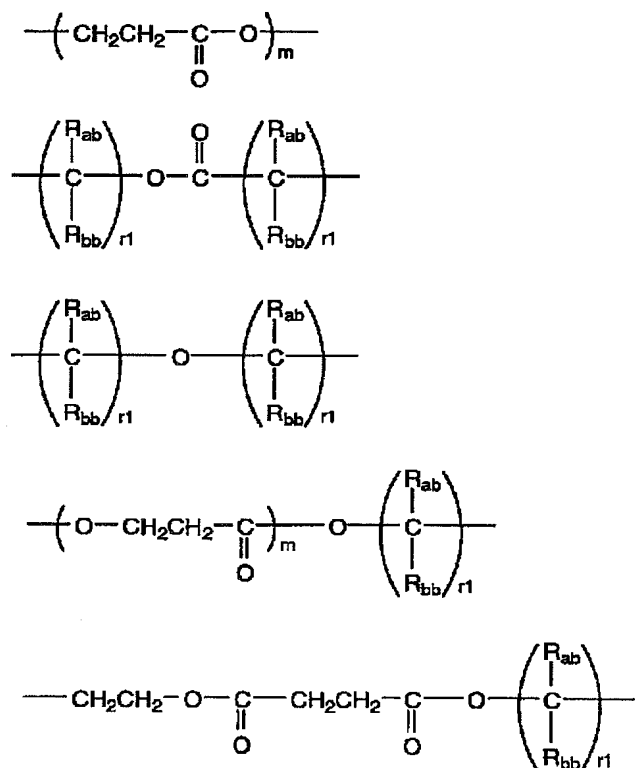
[Formula 71]



[0128] Rb0 expresses the alkyl group of a hydrogen atom, a halogen atom, or carbon numbers 1-4 among a general formula (AI). What was previously illustrated as a desirable substituent which the alkyl group of Rb0 may have the substituent and the alkyl group as R1b in said general formula (V-1) - (V-4) may have as a desirable substituent is mentioned. As a halogen atom of Rb0, a fluorine atom, a chlorine atom, a bromine atom, and iodine atom can be mentioned. Rb0 has a desirable hydrogen atom. B-2 expresses the radical shown by either the general formula (V-1) - (V-4) inside. A' is the same as that of the definition of B in a formula (III). In A', the thing of the following type is mentioned as a this \*\*\*\*\* divalent radical, for example.

[0129]

[Formula 72]



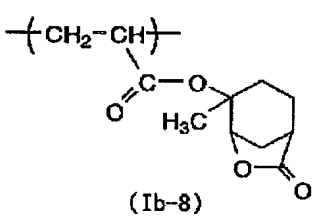
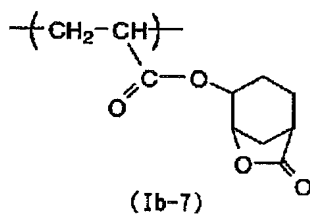
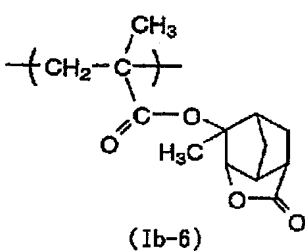
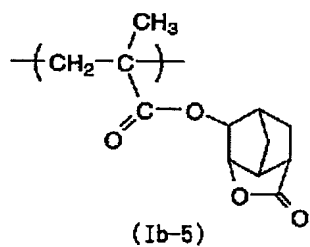
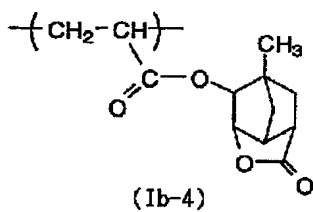
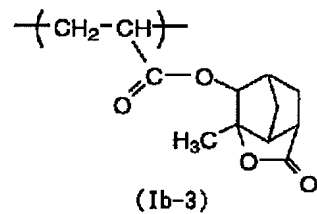
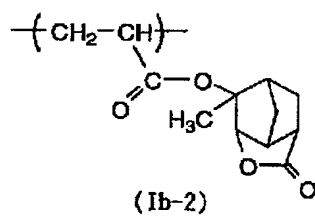
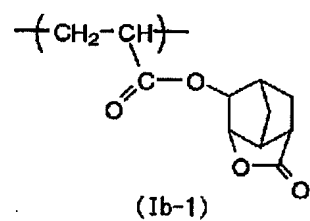
[0130] In the above-mentioned formula, Rab and Rbb express a hydrogen atom, an alkyl group, a permutation alkyl group, a halogen atom, a hydroxyl group, and an alkoxy group, and even if both are the same, they may differ. As an alkyl group, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, and butyl, are chosen from a methyl group, an ethyl group, a propyl group, and an isopropyl group desirable still more preferably. As a substituent of a permutation alkyl group, the alkoxy group of a hydroxyl group, a halogen atom, and carbon numbers 1-4 can be mentioned. As an alkoxy group, the thing of 1-4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can be mentioned. As a halogen atom, a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc. can be mentioned. r1 -- the integer of 1-10 -- the integer of 1-4 is expressed preferably. m -- the integer of 1-3 -- 1 or 2 is expressed preferably.

[0131] Although the example of the repeat unit expressed with a general formula (AI) below is given, the

contents of this invention are not limited to these.

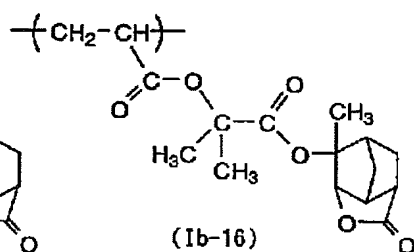
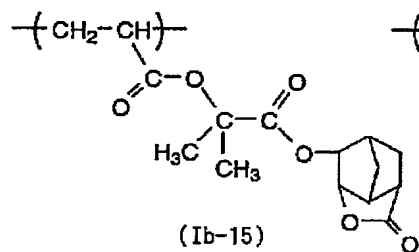
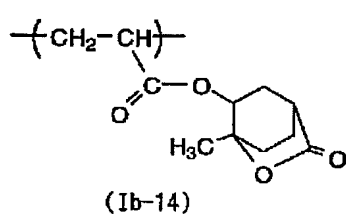
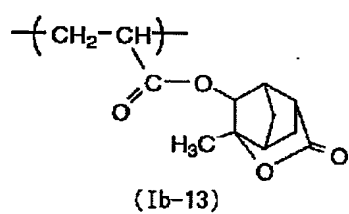
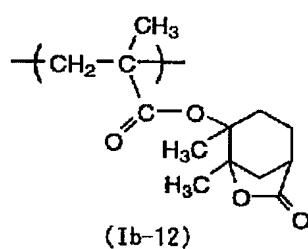
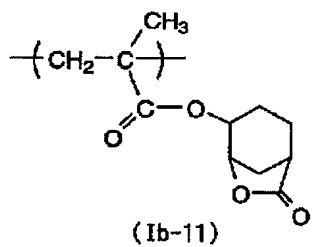
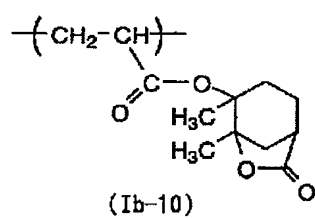
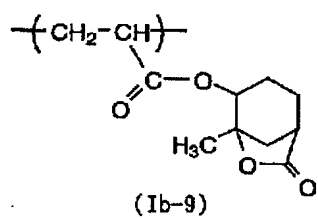
[0132]

[Formula 73]



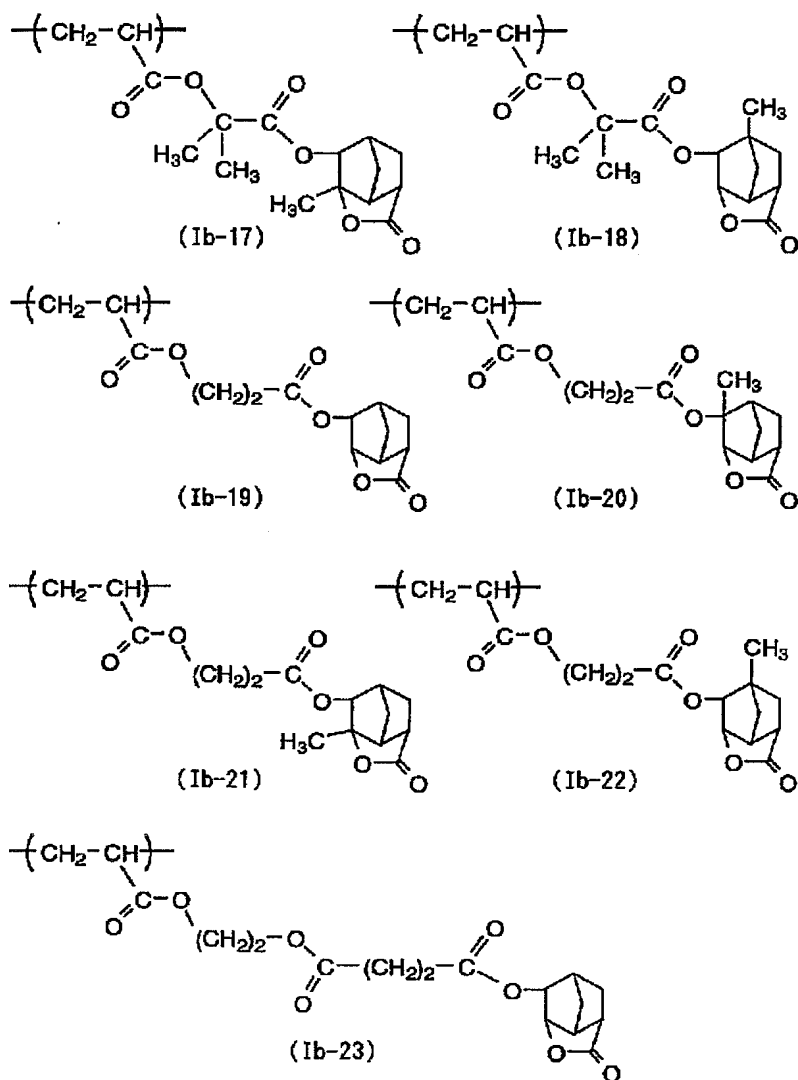
[0133]

[Formula 74]



[0134]

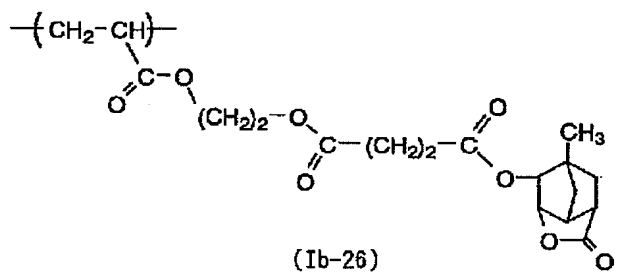
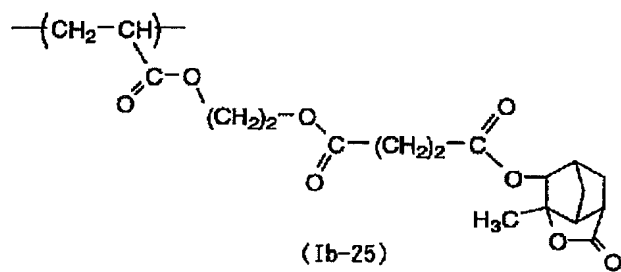
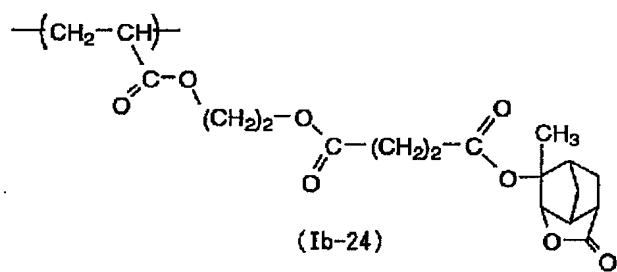
[Formula 75]



[0135]

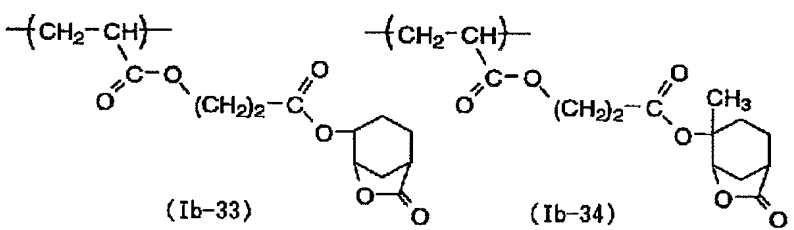
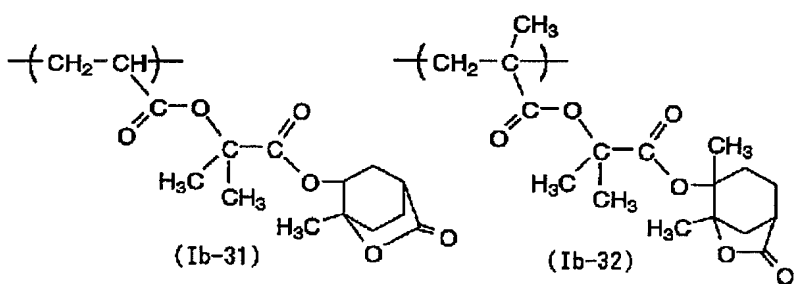
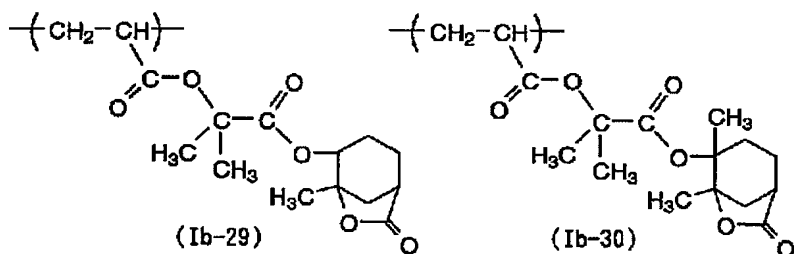
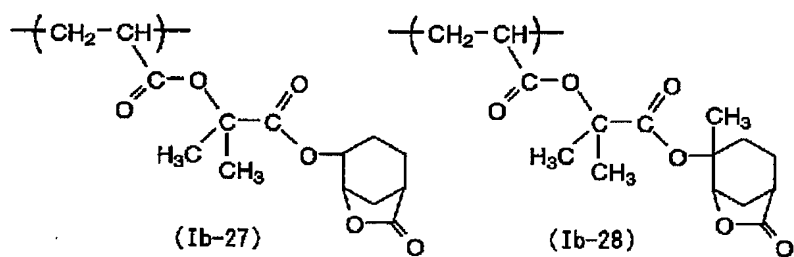
[Formula 76]





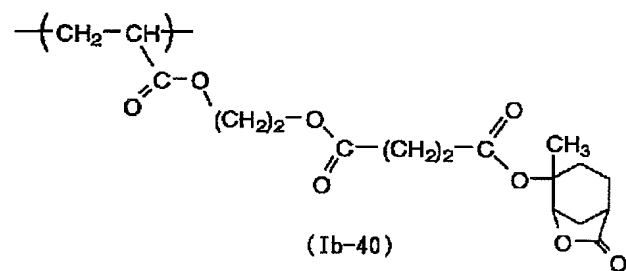
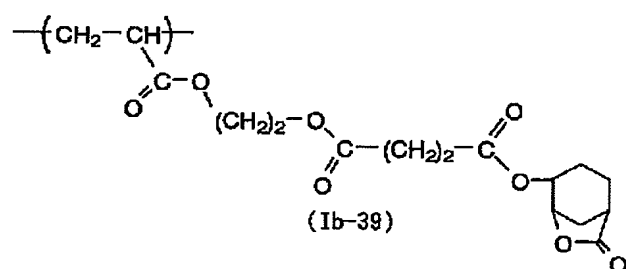
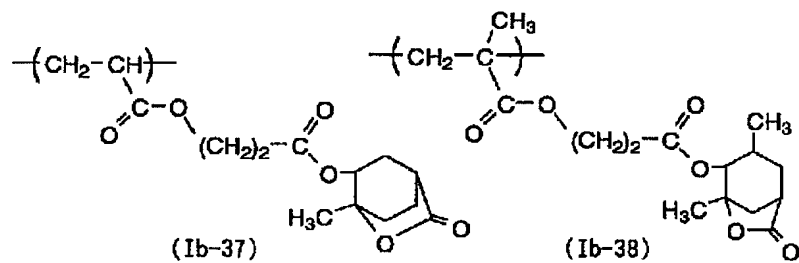
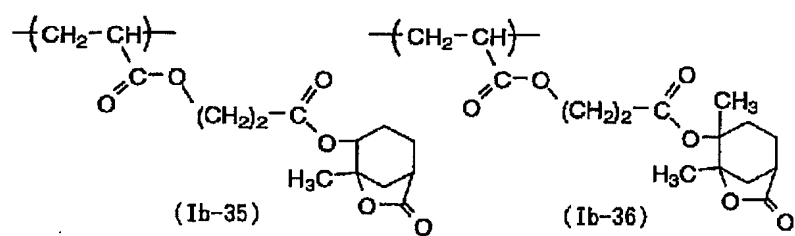
[0136]

[Formula 77]



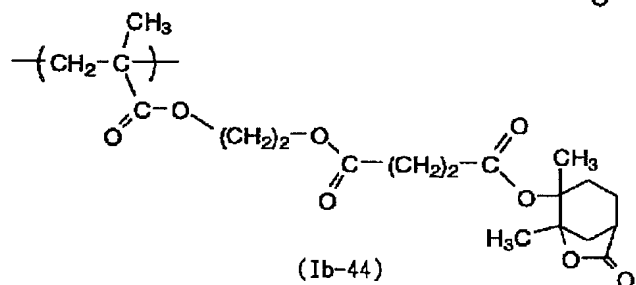
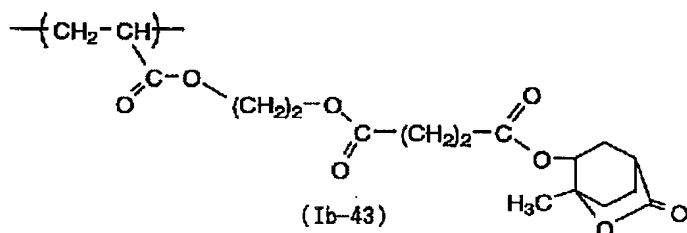
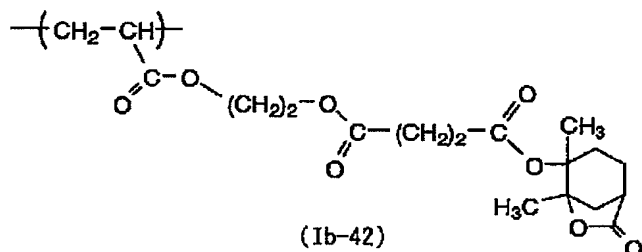
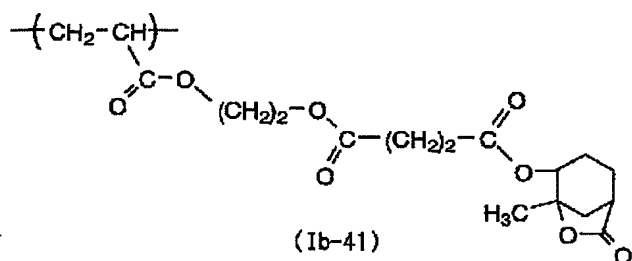
[0137]

[Formula 78]



[0138]

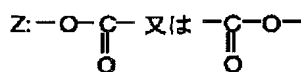
[Formula 79]



[0139] Next, the repeat structural unit which has the structure expressed with the following general formula (VI) is explained.

[0140]

[Formula 80]



[0141] The owner pons type alicyclic ring containing Z may have the substituent. As a substituent, a carboxyl group, a hydroxyl group, a halogen atom, an alkyl group (preferably carbon numbers 1-4), an alkoxy group (preferably carbon numbers 1-4), an alkoxy carbonyl group (preferably carbon numbers 2-5), an acyl group (for example, a formyl group, benzoyl), an acyloxy radical (for example, propyl carbonyloxy group, a

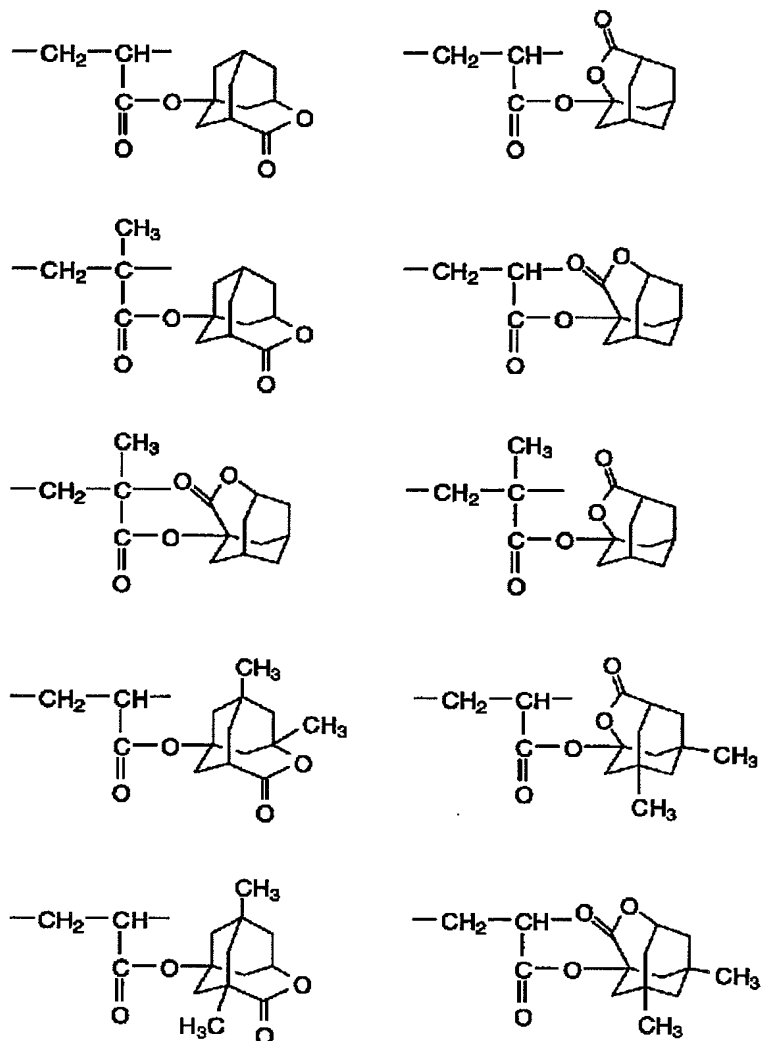
benzoyloxy radical), and an alkyl sulfonyl sulfamoyl group ( $-\text{CONHSO}_2\text{CH}_3$  grade) are mentioned, for example. In addition, the alkyl group as a substituent may be further permuted by the hydroxyl group, the halogen atom, the alkoxy group (preferably carbon numbers 1-4), etc.

[0142] B in a general formula (III) may be combined in which location of the carbon atom which constitutes the owner pons type alicyclic ring structure containing Z in a general formula (VI).

[0143] Although the example of a repeat unit of having the structure expressed with a general formula (VI) below is given, it is not limited to these.

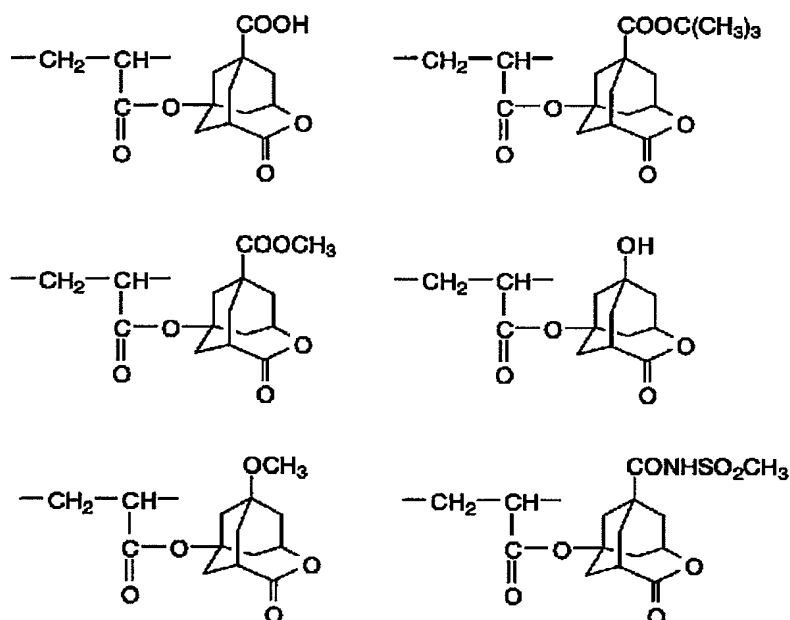
[0144]

[Formula 81]



[0145]

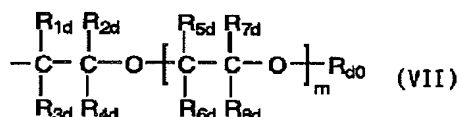
[Formula 82]



[0146] Furthermore, R92 in a formula (III) explains the repeat structural unit which has the structure expressed with the following general formula (VII).

[0147]

[Formula 83]



[0148] In a general formula (VII), R1 d–R8d expresses a hydrogen atom or a chain-like alkyl group independently respectively. Rd0 expresses a hydrogen atom or the shape of a chain, an annular alkyl group, an aryl group, or an aralkyl radical. m expresses the integer of 1–10.

[0149] R1 d–R8 in a general formula (VII) — as a chain-like alkyl group of d and Rd0, the shape of a straight chain, the letter of branching, or an annular alkyl group is mentioned, and you may have the substituent. As an alkyl group of the shape of a straight chain, and the letter of branching, the shape of a straight chain of 1–12 carbon numbers and the letter alkyl group of branching are desirable, are the shape of a straight chain of 1–10 carbon numbers, and a letter alkyl group of branching more preferably, and are a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, t-butyl, a pentyl radical, a hexyl group, a heptyl radical, an octyl radical, a nonyl radical, a decyl group still more preferably As an annular alkyl group of Rd0, the thing of 3–30 carbon numbers is mentioned, and, specifically, a cyclopropyl group, a cyclopentyl group, a cyclohexyl radical, an adamantyl radical, a norbornyl radical, a BORONIRU radical, a tricyclo deca nil radical, a JISHIKURO pentenyl radical, the Novo Renan epoxy group, a menthyl radical, an iso menthyl radical, a neomenthyl radical, a tetracyclo dodecanyl radical, steroid residue, etc. can be mentioned.

[0150] As an aryl group of Rd0, the thing of 6–20 carbon numbers is mentioned, and you may have the substituent. Specifically, a phenyl group, a tolyl group, a naphthyl group, etc. are mentioned. As an aralkyl

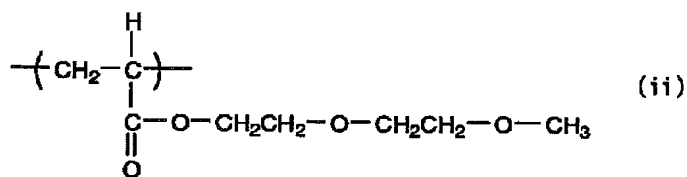
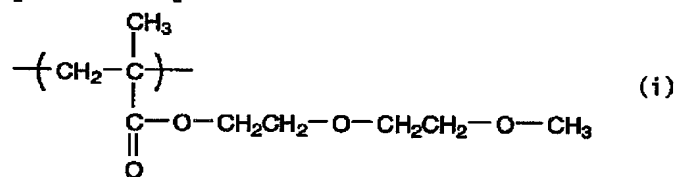
radical of Rd0, the thing of 7-20 carbon numbers is mentioned, and you may have the substituent. Benzyl, a phenethyl radical, a cumyl radical, etc. are mentioned. In this invention, a hydrogen atom and a methyl group are desirable as R1 d-R8d. As Rd0, a hydrogen atom and the alkyl group of 1-4 carbon numbers are desirable. As for m, 1-6 are desirable.

[0151] As further substituent in an above-mentioned shape of chain, annular alkyl group, aryl group, aralkyl radical, alkylene group, annular alkylene group, and arylene radical, a carboxyl group, a cyano group, a hydroxyl group, halogen atoms (for example, a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc.), an alkyl group, a permutation alkyl group, an alkoxy group, alkoxy carbonyl groups (preferably carbon numbers 1-4, for example, a methoxy group, an ethoxy radical, a propoxy group, a butoxy radical, etc.) an acyl group, an acyloxy radical (for example, acetoxyl radical), and an acetyl amide group be mentioned. As an alkyl group, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, a cyclo propyl group, cyclo butyl, and a cyclopentyl group, can be mentioned here. As a substituent of a permutation alkyl group, a hydroxyl group, a halogen atom, and an alkoxy group (preferably carbon numbers 1-4) can be mentioned.

[0152] Although the example of a repeat unit of having the structure expressed with a general formula (VII) below is given, it is not limited to these.

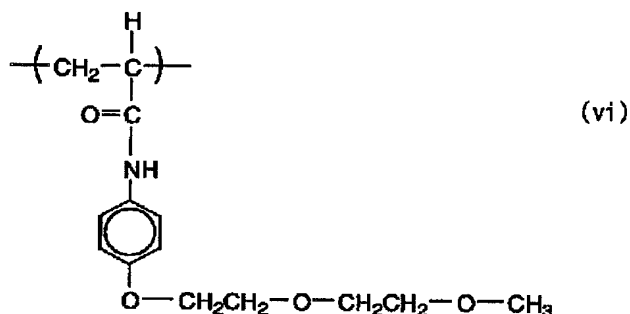
[0153]

[Formula 84]



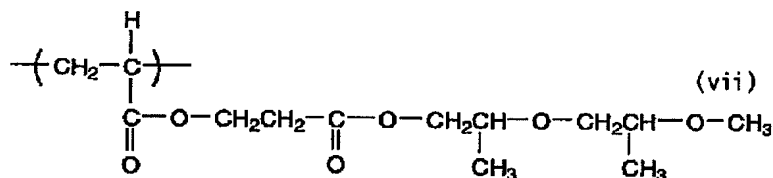
[0154]

[Formula 85]



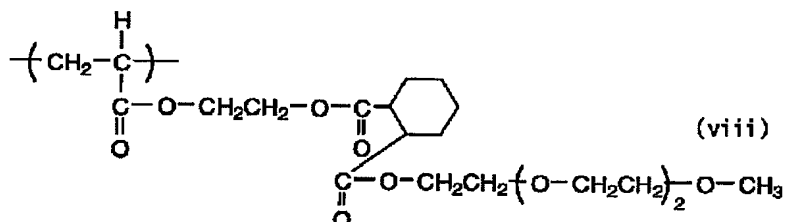
[0155]

[Formula 86]



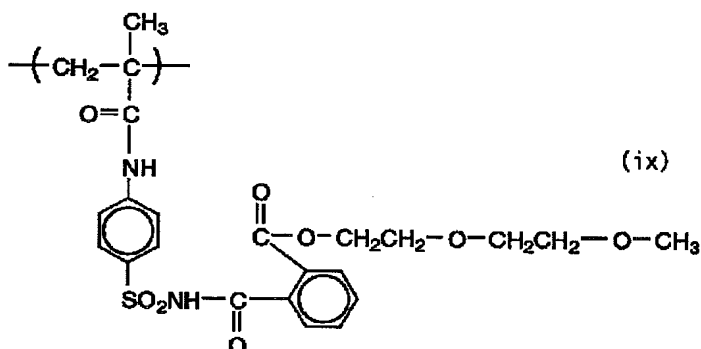
[0156]

[Formula 87]



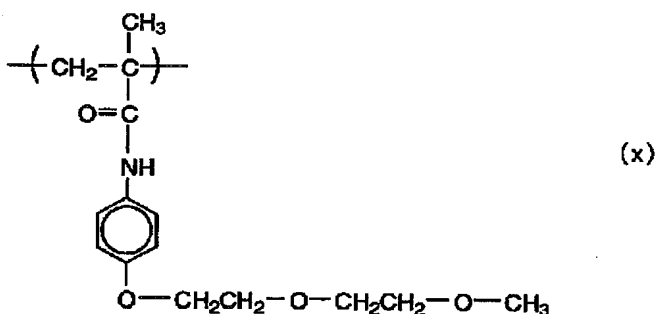
[0157]

[Formula 88]



[0158]

[Formula 89]



[0159] Next, R92 in a formula (III) explains the repeat structural unit which has the structure expressed with the following general formula (VIII).

– N+ (R95) (R96) (R97) and X– (VIII) [0160] Inside of a general formula (VIII): R95–R97 express a hydrogen atom, shape of chain, annular alkyl group, and alkenyl radical, an aryl group, or an aralkyl radical independently respectively. However, it may join together mutually and R95–R97 may form a non-ring and a ring. As a chain-like alkyl group, the alkyl group of the shape of a straight chain and the letter of branching is



mentioned, and you may have the substituent. The shape of a straight chain of 1–12 carbon numbers and the letter alkyl group of branching are desirable, are the shape of a straight chain of 1–10 carbon numbers, and a letter alkyl group of branching more preferably, and are a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, a pentyl radical, a neopentyl radical, a hexyl group, a heptyl radical, an octyl radical, a nonyl radical, and a decyl group still more preferably.

[0161] As an annular alkyl group, the thing of 3–30 carbon numbers is mentioned, and hetero atoms, such as an oxygen atom and a nitrogen atom, may be included. Specifically, a cyclo propyl group, a cyclopentyl group, a cyclohexyl radical, an adamantyl radical, a norbornyl radical, a BORONIRU radical, a tricyclo deca nil radical, a JISHIKURO pentenyl radical, the Novo Renan epoxy group, a menthyl radical, an iso menthyl radical, a neomenthyl radical, a tetracyclo dodecanyl radical, steroid residue, a tetrahydropyranyl group, a morpholino radical, etc. can be mentioned.

[0162] As an alkenyl radical, the alkenyl radical of 2–6 carbon numbers is mentioned, and you may have the substituent. Specifically, a vinyl group, a propenyl radical, an allyl group, a butenyl group, a pentenyl radical, a hexenyl radical, a cyclo pentenyl radical, a cyclohexenyl group, a 3-oxo-cyclohexenyl group, a 3-oxo-cyclo pentenyl radical, a 3-oxo-indenyl group, etc. are mentioned. The annular alkenyl radical may contain the oxygen atom among these. As an aryl group, the thing of 6–10 carbon numbers is mentioned, and you may have the substituent. Specifically, a phenyl group, a tolyl group, a naphthyl group, etc. are mentioned.

[0163] As an aralkyl radical, benzyl, a phenethyl radical, a naphthyl methyl group, a naphthyl ethyl group, and a mesityl methyl group can be mentioned.

[0164] A shape [ as R95–R97 ] of chain, annular alkyl group, and alkenyl radical, an aryl group, or as a substituent which the aralkyl radical and the non-ring which R95–R97 may combine and form, and the ring may have for example, a carboxyl group, a cyano group, a hydroxyl group, and a halogen atom (a chlorine atom —) alkoxy groups (desirable — carbon numbers 1–4, for example, a methoxy group, —), such as a bromine atom, a fluorine atom, and iodine atom An ethoxy radical, a propoxy group, a butoxy radical, an acetyl amide group, an alkoxy carbonyl group, An acyl group (preferably carbon numbers 2–10, for example, a formyl group, an acetyl group, a propionyl radical), an acyloxy radical, preferably carbon numbers 2–10, for example, an acetoxyl radical, and an aryl group, preferably carbon numbers 6–14, for example, a phenyl group, are mentioned. About the non-ring and ring which the aryl group as R95–R97 or an aralkyl radical, and R95–R97 may combine and form, you may have alkyl groups (preferably carbon numbers 1–5, for example, a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, a cyclo propyl group, cyclo butyl, a cyclopentyl group, etc.) as a substituent. The alkyl group as this substituent may have substituents, such as a hydroxyl group, a halogen atom, and an alkoxy group (preferably carbon numbers 1–4, for example, a methoxy group, an ethoxy radical, a propoxy group, a butoxy radical), further.

[0165] X<sup>-</sup> has specific structure R-SO<sub>3</sub><sup>-</sup> as mentioned above. The aliphatic hydrocarbon radical of R is the straight chain of 1–20 carbon numbers, a branching alkyl group, or an annular alkyl group preferably, and may have the substituent. Moreover, the aromatic hydrocarbon radical of R is an aromatic series radical of carbon numbers 6–14 preferably, and may have the substituent.

[0166] The methyl group which may have a substituent as an alkyl group of the above-mentioned R, An ethyl group, a propyl group, n-butyl, n-pentyl radical, n-hexyl group, n-octyl radical, a 2-ethylhexyl radical, a decyl group, the dodecyl, etc. are mentioned. As an annular alkyl group The cyclopentyl group and cyclohexyl

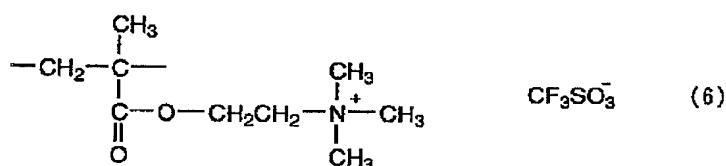
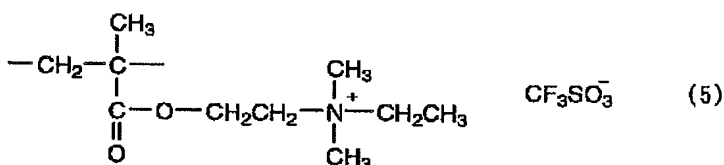
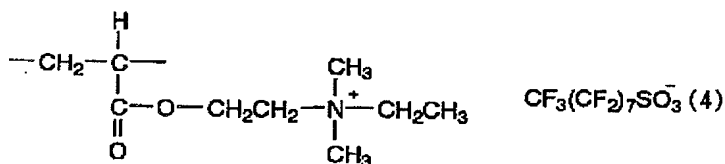
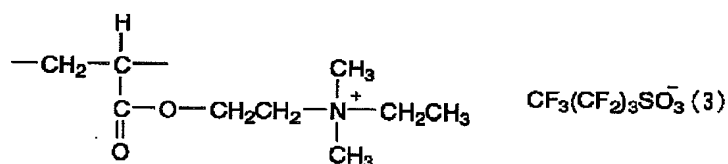
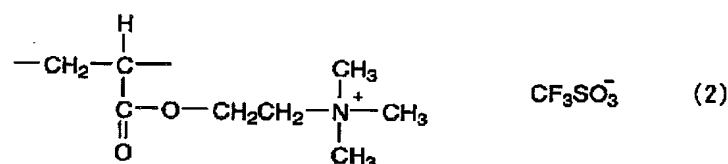
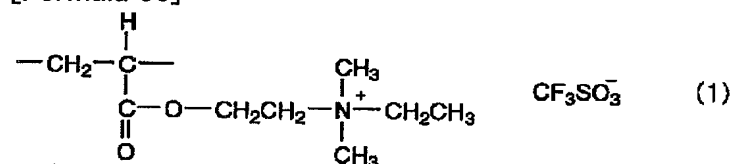
radical which may have a substituent, a cyclo octyl radical, the cyclo dodecyl, an adamantyl radical, a norbornyl radical, a camphor radical, a tricyclo deca nil radical, a menthyl radical, etc. can be mentioned. As an aromatic series radical, a phenyl group, a naphthyl group, etc. which may have a substituent can be mentioned.

[0167] As a substituent which the above-mentioned aliphatic hydrocarbon radical and an aromatic hydrocarbon radical may have, a halogen atom, a hydroxyl group, an alkoxy group, an alkoxy carbonyl group, a camphor radical, etc. are mentioned, and, specifically, a methyl group, t-butyl, a methoxy group, an ethoxy radical, a t-butoxy radical, a fluorine atom, a chlorine atom, a bromine atom, a cyano group, a hydroxyl group, a methoxycarbonyl group, an ethoxycarbonyl radical, a t-butoxycarbonyl group, t-friend ROKISHI carbonyl group, etc. are mentioned, for example. Furthermore, about an aryl group (preferably carbon numbers 6-14) and an aromatic hydrocarbon radical, an alkyl group (carbon numbers 1-15) can be mentioned [ radical / aliphatic hydrocarbon ] as a substituent.

[0168] The example of a repeat unit of having hereafter the structure expressed with a general formula (VIII) is shown. However, the contents of this invention are not limited to these.

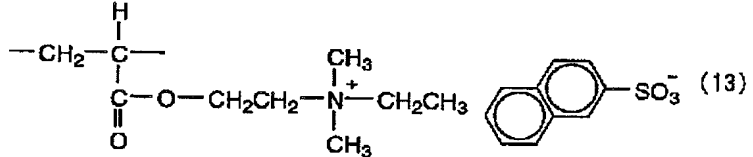
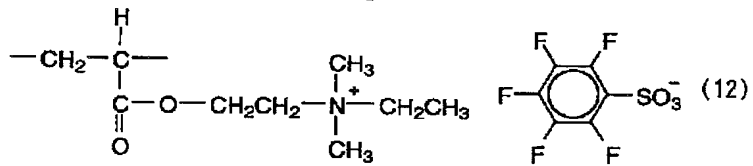
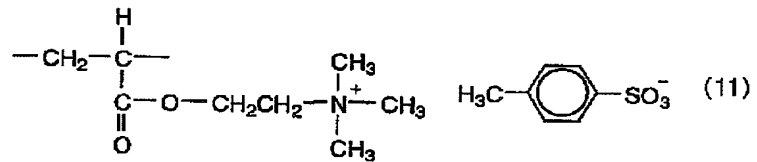
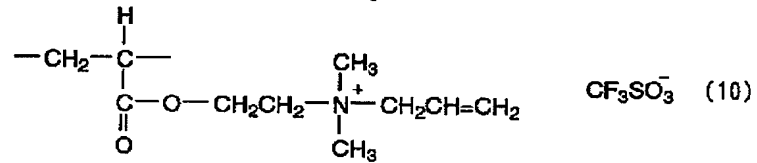
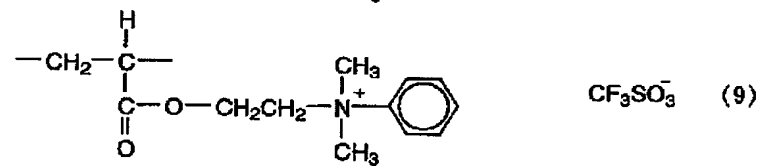
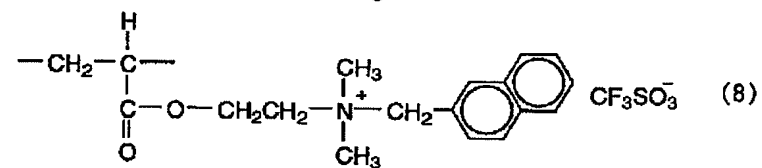
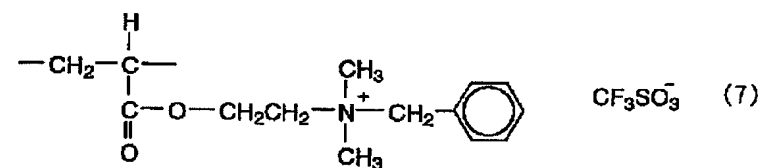
[0169]

[Formula 90]



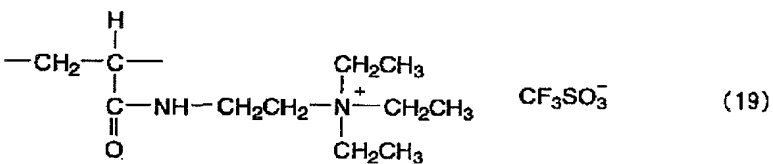
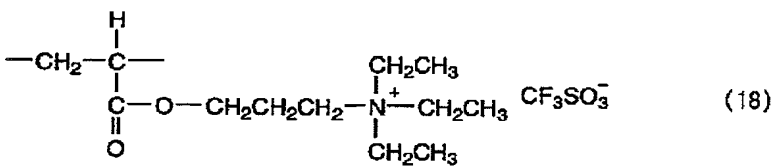
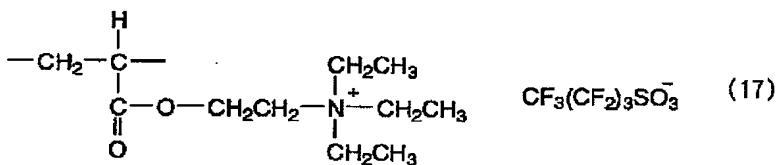
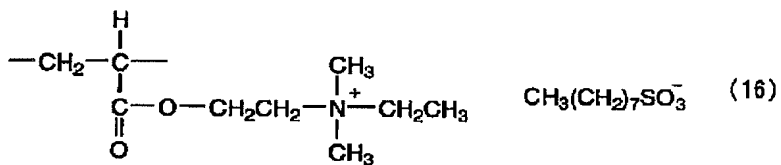
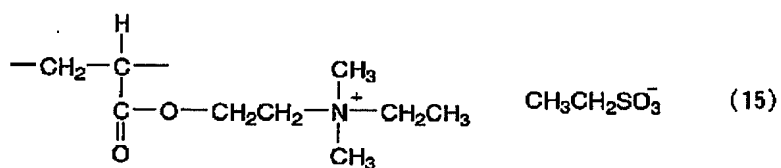
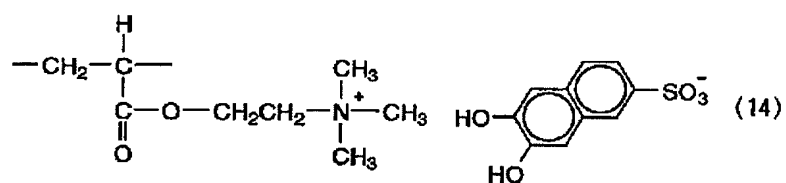
[0170]

[Formula 91]



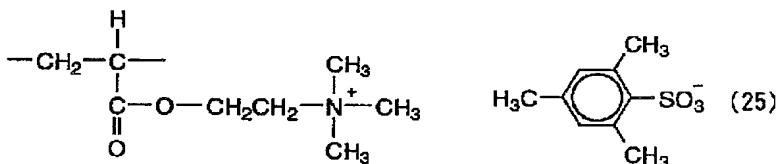
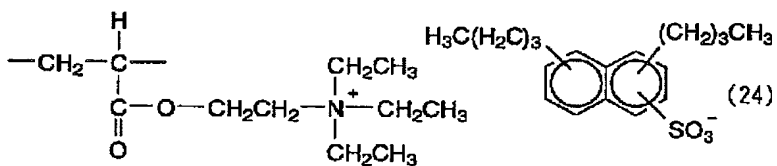
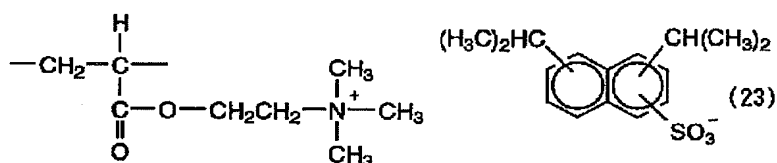
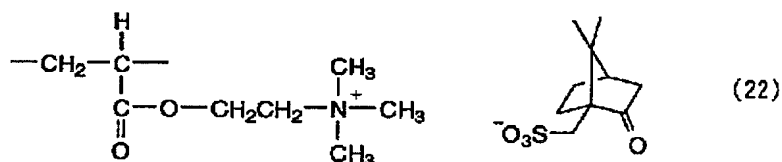
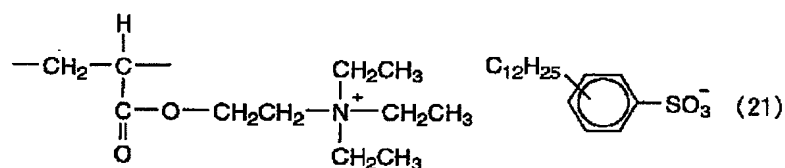
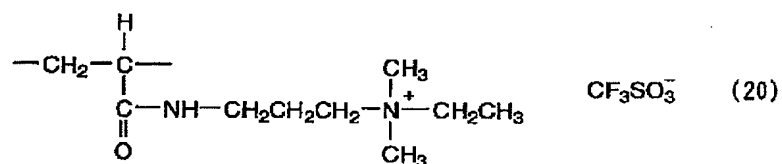
[0171]

[Formula 92]



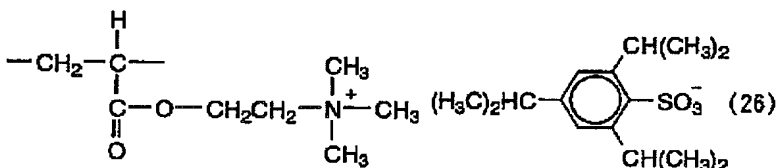
[0172]

[Formula 93]



[0173]

[Formula 94]



[0174] Furthermore, R92 in a formula (III) explains the repeat structural unit which has the structure expressed with the following general formula (IX) or (X).

-R98-A50-R99 (IX)

-SO<sub>3</sub>R100 (X)

[0175] R98 expresses single bond, an alkylene group, an arylene radical, or the divalent radical that combined these among a general formula (IX). As an arylene radical, the thing of carbon numbers 6-10 is mentioned, and you may have the substituent. Specifically, a phenylene group, a tolylene radical, a naphthylene radical,

etc. are mentioned.

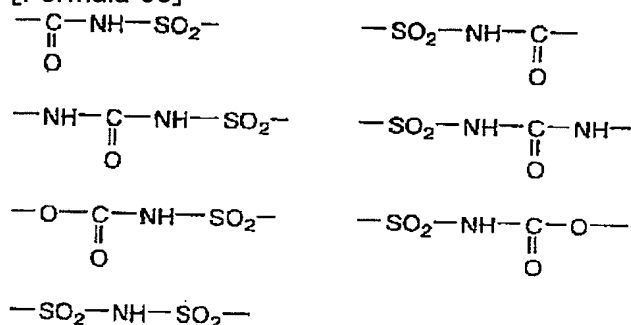
[0176] The radical shown below can be mentioned as an alkylene group.

– Inside of a [C (Rf) and (Rg)] r-type, Rf, Rg : expressing a hydrogen atom, an alkyl group, a permutation alkyl group, a halogen atom, a hydroxyl group, and an alkoxy group, even if both are the same, they may differ, and they express the substituent chosen from the group which low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, and butyl, become from a methyl group, an ethyl group, a propyl group and an isopropyl group desirable still more preferably as an alkyl group. As a substituent of a permutation alkyl group, a hydroxyl group, a halogen atom, and an alkoxy group can be mentioned. As an alkoxy group, the thing of 1–4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can be mentioned. r expresses the integer of 1–10. In the above, a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc. can be mentioned as a halogen atom.

[0177] A50 expresses either of the functional groups shown below.

[0178]

[Formula 95]



[0179] R99 expresses a hydrogen atom or an alkyl group. the chain-like alkyl group of R99 -- the shape of a straight chain, and the letter of branching -- any are sufficient and you may have the substituent. As an alkyl group of the shape of a straight chain, and the letter of branching, the thing of carbon numbers 1–12 is desirable, is a thing of carbon numbers 1–10 more preferably, and can mention preferably a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, t-butyl, a pentyl radical, a hexyl group, a heptyl radical, an octyl radical, a nonyl radical, and a decyl group concretely.

[0180] R100 in a general formula (X) may express the shape of a chain, an annular alkyl group, an aryl group, or an aralkyl radical, and may have the substituent. the chain-like alkyl group of R100 -- the shape of a straight chain, and the letter of branching -- any are sufficient and you may have the substituent. As an alkyl group of the shape of a straight chain, and the letter of branching, the thing of carbon numbers 1–12 is desirable, is a thing of carbon numbers 1–10 more preferably, and can mention preferably a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, t-butyl, a pentyl radical, a hexyl group, a heptyl radical, an octyl radical, a nonyl radical, and a decyl group concretely. As an annular alkyl group of R100, the thing of carbon numbers 3–30 is mentioned, and, specifically, a cyclo propyl group, a cyclopentyl group, a cyclohexyl radical, an adamantyl radical, a norbornyl radical, a BORONIRU radical, a tricyclo deca nil radical, a JISHIKURO pentenyl radical, the Novo Renan epoxy group, a menthyl radical, an iso menthyl radical, a neomenthyl radical, a tetracyclo dodecanyl radical, steroid residue, etc. can be mentioned. The ring structure may have a hetero atom and double association. Tetrahydropyran and a

pentene ring can be mentioned as such an example.

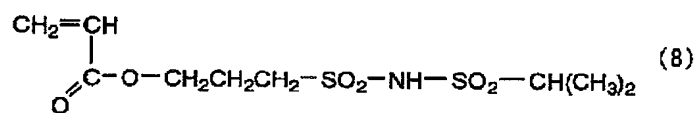
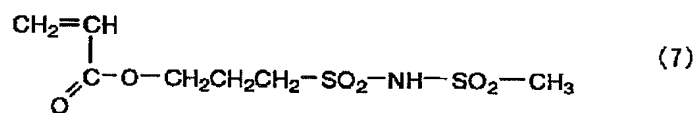
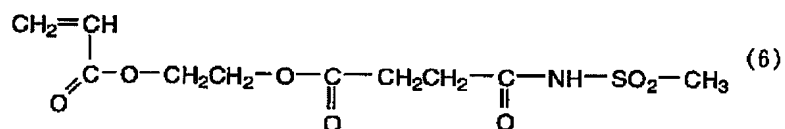
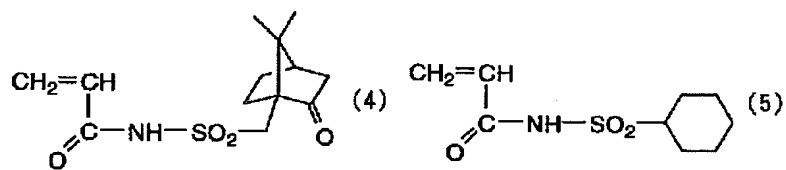
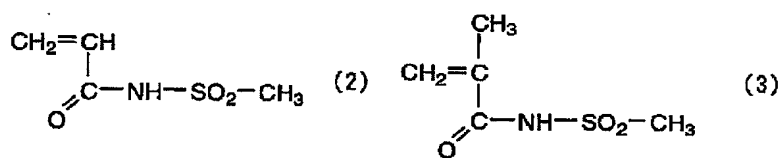
[0181] As an aryl group of R100, the thing of carbon numbers 6–20 is mentioned, and you may have the substituent. Specifically, a phenyl group, a tolyl group, a naphthyl group, etc. are mentioned. As an aralkyl radical of R100, the thing of carbon numbers 7–20 is mentioned, and you may have the substituent. Specifically, benzyl, a phenethyl radical, a cumyl radical, etc. are mentioned.

[0182] As a substituent which the chain-like alkyl group of R99, the shape of a chain of R100, the annular alkyl group, the alkoxy group, the aryl group, or the aralkyl radical may have for example, a carboxyl group, a cyano group, a hydroxyl group, and a halogen atom (a chlorine atom —) alkoxy groups (desirable — carbon numbers 1–4, for example, a methoxy group, —), such as a bromine atom, a fluorine atom, and iodine atom. An ethoxy radical, a propoxy group, a butoxy radical, an acetyl amide group, an alkoxy carbonyl group, An acyl group (preferably carbon numbers 2–10, for example, a formyl group, an acetyl group, a propionyl radical), an acyloxy radical, preferably carbon numbers 2–10, for example, an acetoxy radical, and an aryl group, preferably carbon numbers 6–14, for example, a phenyl group, are mentioned. About the aryl group or the aralkyl radical, you may have alkyl groups (preferably carbon numbers 1–5, for example, a methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, a cyclo propyl group, cyclo butyl, a cyclopentyl group, etc.) further as a substituent as R100. The alkyl group as this substituent may have substituents, such as a hydroxyl group, a halogen atom, and an alkoxy group (preferably carbon numbers 1–4, for example, a methoxy group, an ethoxy radical, a propoxy group, a butoxy radical), further. In addition, a ring structure may form the condensed ring.

[0183] Although example (2) example [ of the monomer equivalent to the repeat structural unit which has – (5) and the structure shown by the general formula (IX) ] (6) – (15) of the monomer corresponding to the repeat unit hereafter expressed with the general formula (III) containing –NH–SO<sub>2</sub>– is shown, it is not limited to these.

[0184]

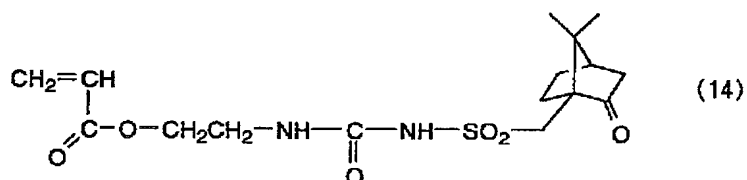
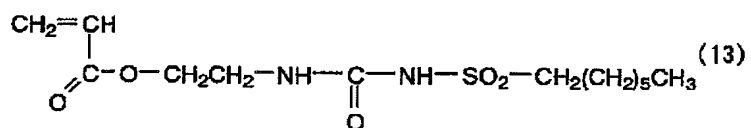
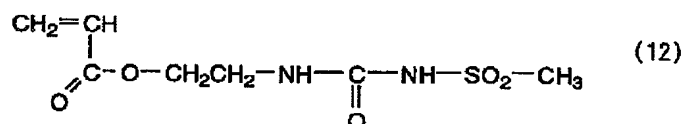
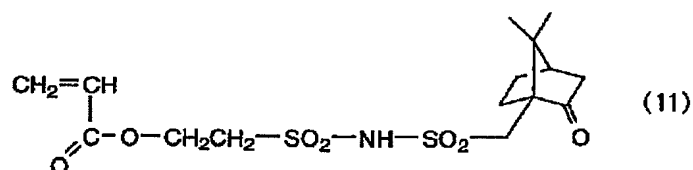
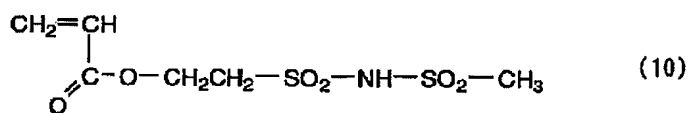
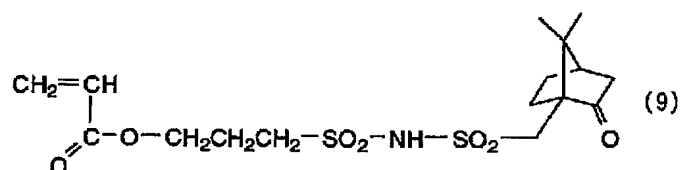
[Formula 96]



[0185]

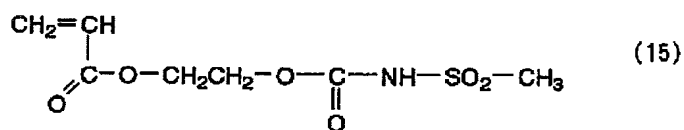
[Formula 97]





[0186]

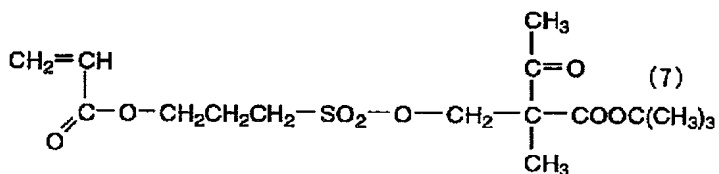
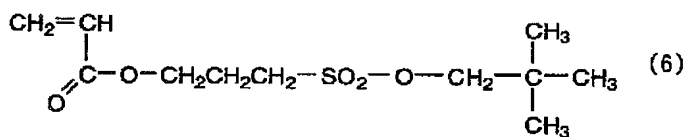
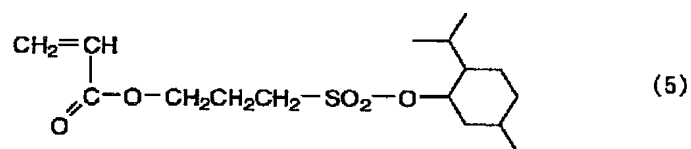
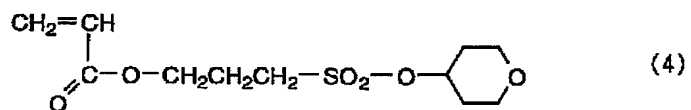
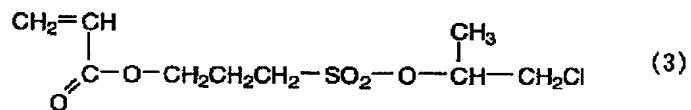
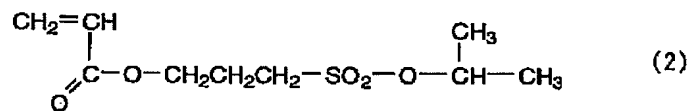
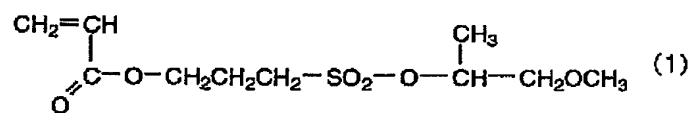
[Formula 98]



[0187] Although the example of the monomer equivalent to the repeat structural unit which has hereafter the structure expressed with a general formula (X) is shown, it is not limited to these.

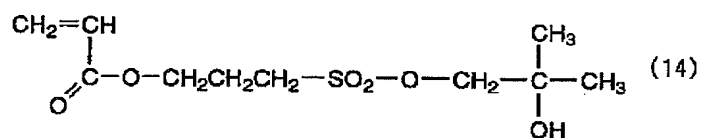
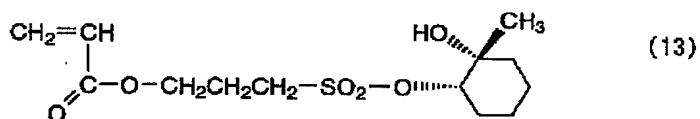
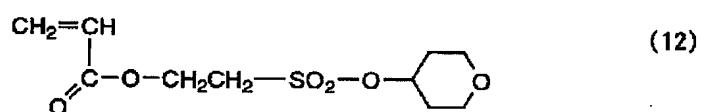
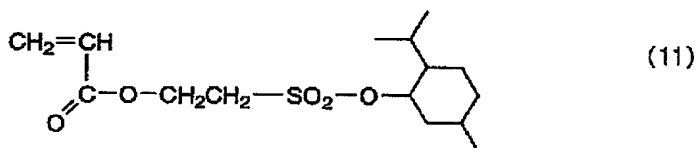
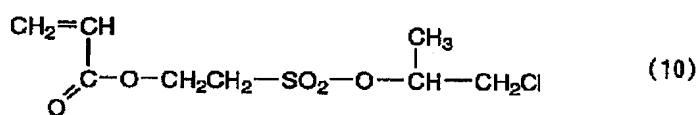
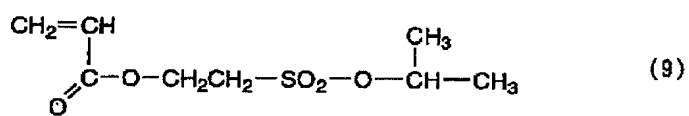
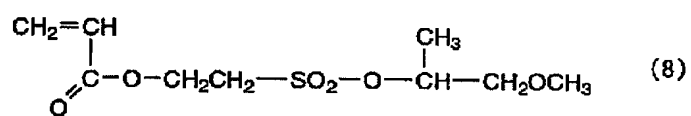
[0188]

[Formula 99]



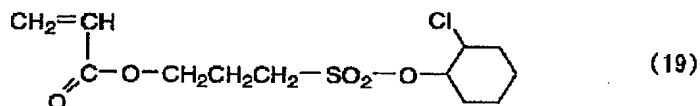
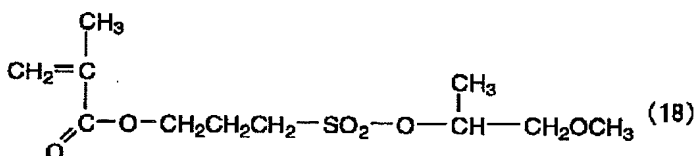
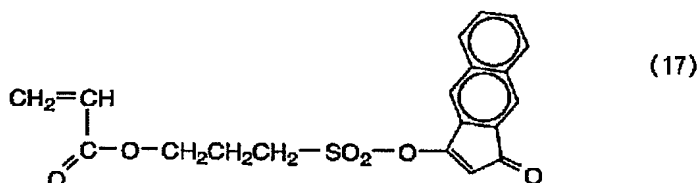
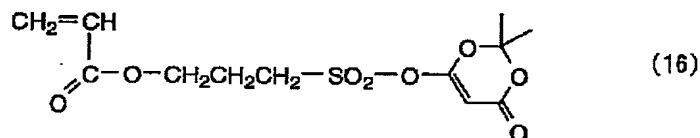
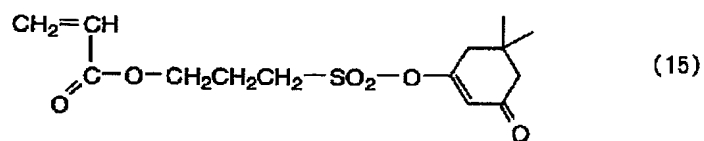
[0189]

[Formula 100]



[0190]

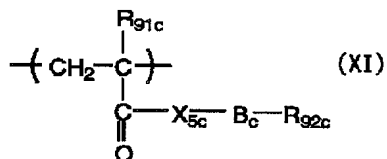
[Formula 101]



[0191] The acidolysis nature resin used by this invention can also contain further the repeat unit expressed with the following type (XI).

[0192]

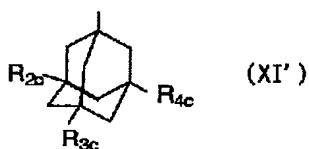
[Formula 102]



[0193] R<sub>91c</sub>, X<sub>5c</sub>, R<sub>93c</sub>, and B<sub>c</sub> are the same as that of R<sub>91</sub>, X<sub>5</sub>, R<sub>93</sub>, and B about the above-mentioned general formula (III) respectively about a general formula (XI). R<sub>92c</sub> expresses the radical expressed with the following general formula (XI').

[0194]

[Formula 103]



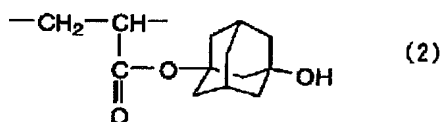
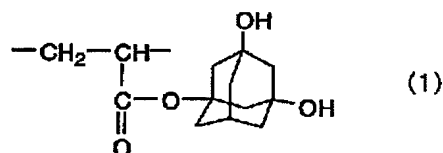
[0195] In a general formula (XI'), R2 c-R4c expresses a hydrogen atom or a hydroxyl group independently respectively. However, at least one of R2 c-R4c expresses a hydroxyl group.

[0196] The structures expressed with a general formula (XI) are a dihydroxy object and a mono-hydroxy object preferably, and are dihydroxy objects more preferably.

[0197] Although the example of a repeat unit of having the structure expressed with a general formula (XI) below is given, it is not limited to these.

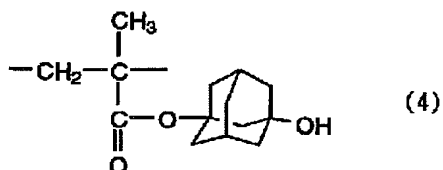
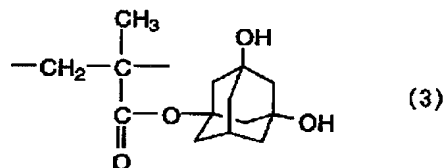
[0198]

[Formula 104]



[0199]

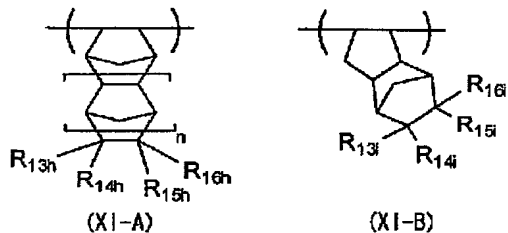
[Formula 105]



[0200] Further following general formula (XI-A) or (XI-B) repeat unit expressed can be made to contain in the resin concerning this invention.

[0201]

[Formula 106]



[0202] Inside of the above-mentioned general formula (XI-A) R13 h-R16h expresses respectively the alkyl

group or cyclic-hydrocarbon radical which may have a hydrogen atom, a halogen atom, a cyano group,  $-\text{COOH}$ ,  $-\text{COOR17h}$ ,  $-\text{C(=O)-Xh-Ah-R18h}$ , or a substituent independently. Moreover, at least two of R13 h-R16h may join together, and a ring may be formed. n expresses 0 or 1. However, no R13 h-R16h has the radical decomposed with an acid. R17h, the alkyl group and cyclic-hydrocarbon radical which may have the substituent, or the  $-\text{Y}$  aforementioned sets are expressed. Xh expresses an oxygen atom, a sulfur atom,  $-\text{NH}-$ ,  $-\text{NHSO}_2-$ , or  $-\text{NHSO}_2\text{NH}-$ . Ah expresses single bond or a divalent connection radical. R18h, the alkoxy group which may have  $-\text{COOH}$ ,  $-\text{COOR17h}$ ,  $-\text{CN}$ , the hydroxyl group, and the substituent,  $-\text{CO-NH-R19h}$ ,  $-\text{CO-NH-SO}_2\text{-R19h}$ , or the  $-\text{Y}$  aforementioned sets are expressed. R19h, the alkyl group or cyclic-hydrocarbon radical which may have the substituent is expressed.

[0203] As a halogen atom in the above-mentioned R13 h-R16h, a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc. can be mentioned.

[0204] As an alkyl group in the above-mentioned R13 h-R16h, the shape of a straight chain of 1-10 carbon numbers and the letter alkyl group of branching are desirable, are the shape of a straight chain of 1-6 carbon numbers, and a letter alkyl group of branching more preferably, and are a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, and t-butyl still more preferably.

[0205] As a cyclic-hydrocarbon radical in the above-mentioned R13 h-R16h, it is an annular alkyl group and owner pons type hydrocarbon, for example, and a cyclo propyl group, a cyclopentyl group, a cyclohexyl radical, an adamantyl radical, a 2-methyl-2-adamantyl radical, a norbornyl radical, a BORONIRU radical, an isoboronyl radical, a tricyclo deca nil radical, a JISHIKURO pentenyl radical, the Novo Renan epoxy group, a menthyl radical, an iso menthyl radical, a neomenthyl radical, a tetracyclo dodecanyl radical, etc. can be mentioned. As a ring which at least two of the above-mentioned R13 h-R16h combine and form, the ring of the carbon numbers 5-12, such as cyclopentene, a cyclohexene, cycloheptane, and cyclooctane, is mentioned.

[0206] As an alkoxy group in the above-mentioned R18h, the thing of 1-4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can be mentioned.

[0207] As further substituent in the above-mentioned alkyl group, a cyclic-hydrocarbon radical, and an alkoxy group, a hydroxyl group, a halogen atom, a carboxyl group, an alkoxy group, an acyl group, a cyano group, an acyloxy radical, etc. can be mentioned. As a halogen atom, a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc. can be mentioned. As an alkoxy group, the thing of 1-4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can mention, a formyl group, an acetyl group, etc. can be mentioned as an acyl group, and an acetoxy radical etc. can be mentioned as an acyloxy radical.

[0208] The combination of independent [ which is chosen from the group which consists of single bond, an alkylene group, a permutation alkylene group, an ether group, a thioether radical, a carbonyl group, an ester group, an amide group, a sulfonamide radical a urethane group, and an urea radical as a divalent connection radical of Above Ah ], or two radicals or more is mentioned.

[0209] The radical expressed with the following formula can be mentioned as the alkylene group in Above Ah, and a permutation alkylene group.

- Rbh and Rch express a hydrogen atom, an alkyl group, a permutation alkyl group, a halogen atom, a hydroxyl group, and an alkoxy group among a  $[\text{C(Rbh)}]$  (Rch) r-type, and even if both are the same, they may

differ. As an alkyl group, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, and butyl, are chosen from a methyl group, an ethyl group, a propyl group, and an isopropyl group desirable still more preferably. As a substituent of a permutation alkyl group, a hydroxyl group, a halogen atom, and an alkoxy group can be mentioned. As an alkoxy group, the thing of 1-4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can be mentioned. As a halogen atom, a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc. can be mentioned.  $r$  expresses the integer of 1-10.

[0210] Inside of a general formula (XI-B)  $R_{13}$  i- $R_{16i}$  expresses respectively the alkyl group or cyclic-hydrocarbon radical which may have a hydrogen atom, a halogen atom, a cyano group,  $-COOH$ ,  $-COOR_{17i}$ , the radical decomposed according to an operation of an acid,  $-C(=O)-X_i-A_i-R_{18i}$ , or a substituent independently. Moreover, at least two of  $R_{13}$  i- $R_{16i}$  may join together, and a ring may be formed.  $n$  expresses 0 or 1.  $R_{17i}$  expresses the alkyl group and cyclic-hydrocarbon radical which may have the substituent, or the  $-Y$  aforementioned sets.  $X_i$  expresses an oxygen atom, a sulfur atom,  $-NH-$ ,  $-NHSO_2-$ , or  $-NHSO_2NH-$ .  $A_i$  expresses single bond or a divalent connection radical.  $R_{18i}$  expresses the alkoxy group which may have  $-COOH$ ,  $-COOR_{17i}$ ,  $-CN$ , the hydroxyl group, and the substituent,  $-CO-NH-R_{19i}$ ,  $-CO-NH-SO_2-R_{19i}$ , or the  $-Y$  aforementioned sets.  $R_{19i}$  expresses the alkyl group or cyclic-hydrocarbon radical which may have the substituent.  $R_{21}$ - $R_{30}$  express respectively the alkyl group which may have the hydrogen atom or the substituent independently among the  $-Y$  above-mentioned sets.  $a$  and  $b$  express 1 or 2.

[0211] It is expressed with  $-C(=O)-X_1$  i- $R_{pi}$  as structure of the radical decomposed according to an operation of an acid. As  $R_{pi}$ , among a formula, the 3rd class alkyl groups, such as  $t$ -butyl and  $t$ -amyl group, An isoboronyl radical, 1-ethoxyethyl radical, a 1-butoxy ethyl group, a 1-iso butoxy ethyl group, 1-alkoxy ethyl groups, such as 1-cyclo hexyloxyethyl radical, 1-methoxymethyl radical, Alkoxy methyl groups, such as a 1-ethoxy methyl group, a 3-oxo-alkyl group, A tetrahydropyranyl group, a tetrahydrofuranyl radical, a trialkylsilyl ester group, A 3-oxocyclohexyl ester group, a 2-methyl-2-adamantyl radical, mevalonic lactone residue, a 2-( $\gamma$ -BUCHIRORAKUTO nil oxy-carbonyl)-2-propyl group, etc. can be mentioned.  $X_{1i}$  expresses an oxygen atom, a sulfur atom,  $-NH-$ ,  $-NHSO_2-$ , or  $-NHSO_2NH-$ .

[0212] As a halogen atom in the above-mentioned  $R_{13}$  i- $R_{16i}$ , a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc. can be mentioned.

[0213] As an alkyl group in the above-mentioned  $R_{13}$  i- $R_{16i}$ , the shape of a straight chain of 1-10 carbon numbers and the letter alkyl group of branching are desirable, are the shape of a straight chain of 1-6 carbon numbers, and a letter alkyl group of branching more preferably, and are a methyl group, an ethyl group, a propyl group, an isopropyl group,  $n$ -butyl, an isobutyl radical,  $sec$ -butyl, and  $t$ -butyl still more preferably.

[0214] As a cyclic-hydrocarbon radical in the above-mentioned  $R_{13}$  i- $R_{16i}$ , it is an annular alkyl group and owner pons type hydrocarbon, for example, and a cyclo propyl group, a cyclopentyl group, a cyclohexyl radical, an adamantyl radical, a 2-methyl-2-adamantyl radical, a norbornyl radical, a BORONIRU radical, an isoboronyl radical, a tricyclo deca nil radical, a JISHIKURO pentenyl radical, the Novo Renan epoxy group, a menthyl radical, an iso menthyl radical, a neomenthyl radical, a tetracyclo dodecanyl radical, etc. can be mentioned. As a ring which at least two of the above-mentioned  $R_{13}$  i- $R_{16i}$  combine and form, the ring of the carbon numbers 5-12, such as cyclopentene, a cyclohexene, cycloheptane, and cyclooctane, is

mentioned.

[0215] As an alkoxy group in the above-mentioned R18i, the thing of 1-4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can be mentioned.

[0216] As further substituent in the above-mentioned alkyl group, a cyclic-hydrocarbon radical, and an alkoxy group, a hydroxyl group, a halogen atom, a carboxyl group, an alkoxy group, an acyl group, a cyano group, an acyloxy radical, etc. can be mentioned. As a halogen atom, a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc. can be mentioned. As an alkoxy group, the thing of 1-4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can mention, a formyl group, an acetyl group, etc. can be mentioned as an acyl group, and an acetoxyl radical etc. can be mentioned as an acyloxy radical.

[0217] The combination of independent [ which is chosen from the group which consists of single bond, an alkylene group, a permutation alkylene group, an ether group, a thioether radical, a carbonyl group, an ester group, an amide group, a sulfonamide radical, a urethane group, and an urea radical as a divalent connection radical of Above Ai ], or two radicals or more is mentioned.

[0218] The radical expressed with the following formula can be mentioned as the alkylene group in Above Ai, and a permutation alkylene group.

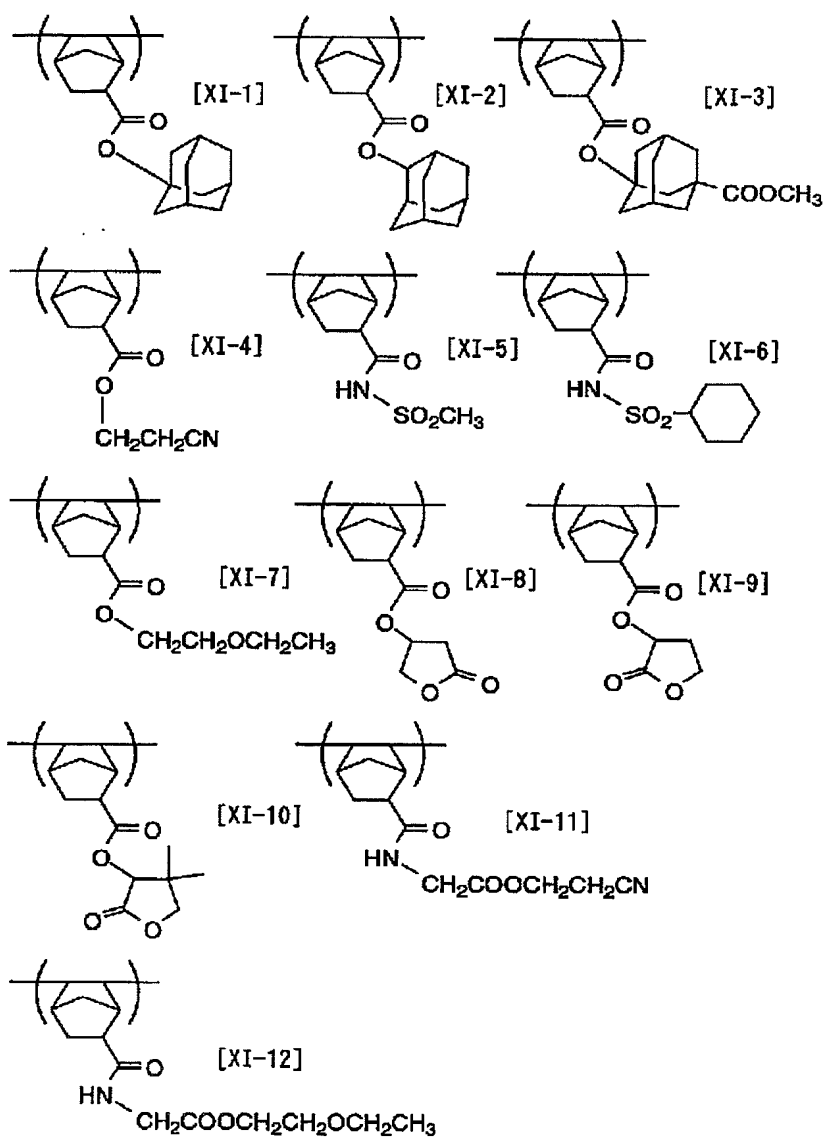
– Rbi and Rci express a hydrogen atom, an alkyl group, a permutation alkyl group, a halogen atom, a hydroxyl group, and an alkoxy group among a [C(Rbi)] (Rci) r-type, and even if both are the same, they may differ. As an alkyl group, low-grade alkyl groups, such as a methyl group, an ethyl group, a propyl group, an isopropyl group, and butyl, are chosen from a methyl group, an ethyl group, a propyl group, and an isopropyl group desirable still more preferably. As a substituent of a permutation alkyl group, a hydroxyl group, a halogen atom, and an alkoxy group can be mentioned. As an alkoxy group, the thing of 1-4 carbon numbers, such as a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical, can be mentioned. As a halogen atom, a chlorine atom, a bromine atom, a fluorine atom, iodine atom, etc. can be mentioned. r expresses the integer of 1-10.

[0219] Although the following following are mentioned as an example of the above-mentioned general formula (XI-A) or (XI-B) the repeat unit expressed, this invention is not limited to these examples.

[0220]

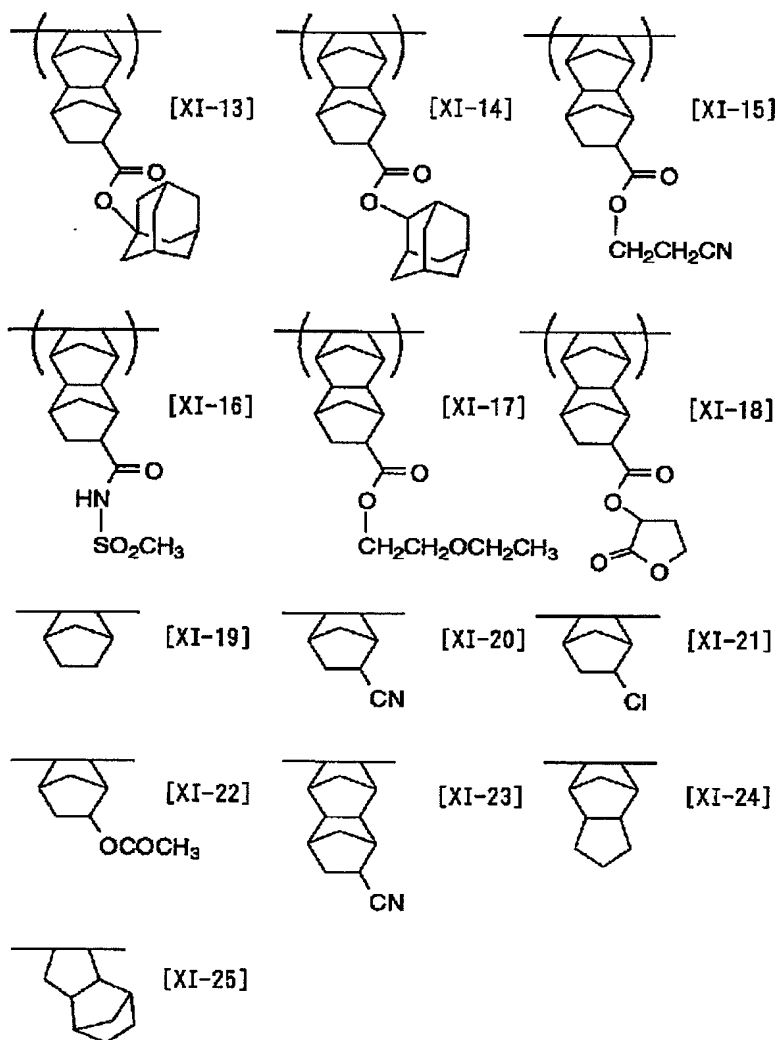
[Formula 107]





[0221]

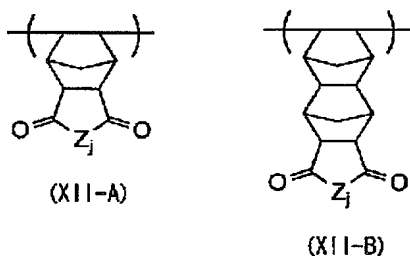
[Formula 108]



[0222] As a desirable copolymerization component which the acidolysis nature resin concerning this invention may also contain further, the following general formula (XII-A) \*\* can mention the repeat unit expressed with (XII-B).

[0223]

[Formula 109]



[0224] Zj expresses an oxygen atom, -NH-, -N(-R50j)-, and -N(-OSO2R50j)- among a formula here, and R50j has semantics [ an alkyl group (permutation) and a cyclic-hydrocarbon (permutation) radical ].

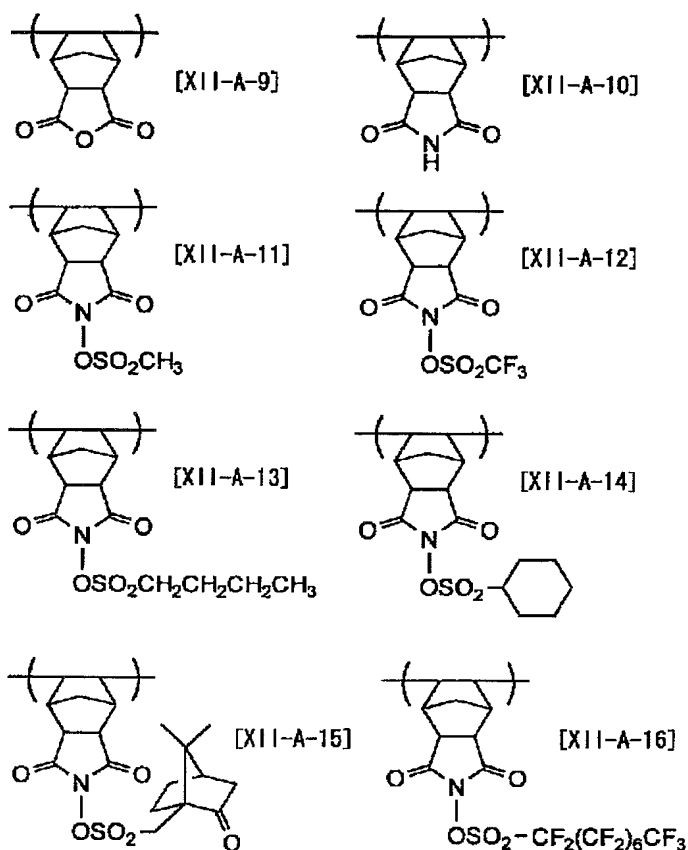
[0225] As an alkyl group in the above-mentioned R50j, the shape of a straight chain of 1-10 carbon numbers and the letter alkyl group of branching are desirable, are the shape of a straight chain of 1-6 carbon numbers,

and a letter alkyl group of branching more preferably, and are a methyl group, an ethyl group, a propyl group, an isopropyl group, n-butyl, an isobutyl radical, sec-butyl, and t-butyl still more preferably.

[0226] As a cyclic-hydrocarbon radical in the above-mentioned R50j, it is an annular alkyl group and owner pons type hydrocarbon, for example, and a cyclo propyl group, a cyclopentylic group, a cyclohexyl radical, an adamantanyl radical, a 2-methyl-2-adamantanyl radical, a norbornyl radical, a BORONIRU radical, an isoboronyl radical, a tricyclo deca nil radical, a JISHIKURO pentenyl radical, the Novo Renan epoxy group, a menthyl radical, an iso menthyl radical, a neomenthyl radical, a tetracyclo dodecanyl radical, etc. can be mentioned. The above-mentioned general formula (XII-A) \*\* is not limited to these examples, although following [XII-A-9] - [XII-A -16] and [XII-B -9] - [XII-B -16] is mentioned as an example of the repeat unit expressed with (XII-B).

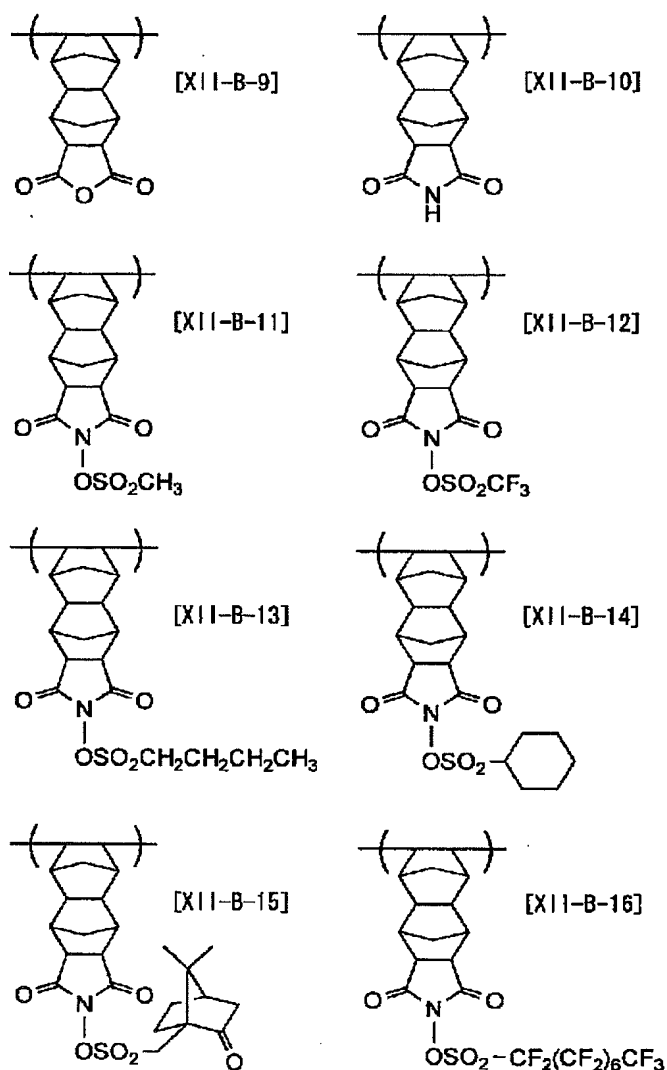
[0227]

[Formula 110]



[0228]

[Formula 111]



[0229] Although copolymerization of the acidolysis nature resin concerning this invention may be carried out as what gives the repeat unit in which the still more nearly following monomers constitute this resin within limits from which the effectiveness of this invention is acquired effectively, it is not limited to the following monomer. Thereby, fine tuning of the adhesion to the substrate of the engine performance required of said resin, the solubility over (1) spreading solvent, (2) film-production nature (glass transition point), (3) alkali development property, (4) \*\*\*\*\* (relative-degree-of-intimacy aquosity, alkali fusibility radical selection), and (5) unexposed parts and (6) dry-etching resistance \*\* is attained especially. The compound which has one addition polymerization nature unsaturated bond chosen from acrylic ester, methacrylic ester, acrylamides, methacrylamide, an allyl compound, vinyl ether, and vinyl ester as such a copolymerization monomer, for example can be mentioned.

[0230] Specifically For example, acrylic ester, for example, alkyl (carbon atomic number of alkyl group has desirable thing of 1-10) acrylate for example, a methyl acrylate, an ethyl acrylate, and acrylic-acid propyl -- Acrylic-acid amyl, acrylic-acid cyclohexyl, acrylic-acid ethylhexyl, Acrylic-acid octyl, acrylic-acid-t-octyl, chlorethyl acrylate, 2-hydroxyethyl acrylate 2, 2-dimethyl hydroxypropyl acrylate, 5-hydroxy pentyl acrylate, trimethylol propane monoacrylate, pentaerythritol monoacrylate, benzyl acrylate, methoxybenzyl acrylate,

furfuryl acrylate, tetrahydrofurfuryl acrylate, etc.;

[0231] methacrylic ester (for example, methyl methacrylate —), for example, alkyl (carbon atomic number of alkyl group has desirable thing of 1–10.) methacrylate Ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, Amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, Benzyl methacrylate, KURORU benzyl methacrylate, octyl methacrylate, 2-hydroxyethyl methacrylate, 4-hydroxy butyl methacrylate, 5-hydroxy pentyl methacrylate, 2, and 2-dimethyl-3-hydroxypropyl methacrylate, Trimethylol propane mono-methacrylate, pentaerythritol mono-methacrylate, furfuryl methacrylate, tetrahydrofurfuryl methacrylate, etc.;

[0232] Acrylamides, for example, acrylamide, N-alkyl acrylamide, (As an alkyl group, there are the thing of the carbon atomic numbers 1–10, for example, a methyl group, an ethyl group, a propyl group, butyl, t-butyl, a heptyl radical, an octyl radical, a cyclohexyl radical, a hydroxyethyl radical, etc.) N and N-dialkyl acrylamide (as an alkyl group, there are the thing of the carbon atomic numbers 1–10, for example, a methyl group, an ethyl group, butyl, an isobutyl radical, an ethylhexyl radical, a cyclohexyl radical, etc.)

N-hydroxyethyl-N-methylacrylamide, N-2-acetamidoethyl-N-acetyl acrylamide, etc.;

[0233] Methacrylamide, for example, methacrylamide, N-alkyl methacrylamide (as alkyl group, there are thing of carbon atomic numbers 1–10, for example, methyl group, ethyl group, t-butyl, ethylhexyl radical, hydroxyethyl radical, cyclohexyl radical, etc.), N, and N-dialkyl methacrylamide (there are an ethyl group, a propyl group, butyl, etc. as an alkyl group.), N-hydroxyethyl-N-methyl methacrylamide, etc.;

[0234] An allyl compound, for example, allyl ester, allyloxy ethanol (for example, an acetic-acid allyl compound, allyl caproate, a caprylic-acid allyl compound, a lauric-acid allyl compound, a palmitic-acid allyl compound, a stearin acid allyl compound, allyl benzoate, an acetoacetic-acid allyl compound, a lactic-acid allyl compound, etc.), etc.;

[0235] vinyl ether (for example, hexyl vinyl ether —), for example, alkyl vinyl ether Octyl vinyl ether, DESHIRU vinyl ether, ethylhexyl vinyl ether, Methoxy ethyl vinyl ether, ethoxyethyl vinyl ether, KURORU ethyl vinyl ether, The 1-methyl -2, 2-dimethyl propyl vinyl ether, 2-ethyl butyl vinyl ether, Hydroxyethyl vinyl ether, diethylene-glycol vinyl ether, Dimethylaminoethyl vinyl ether, diethylamino ethyl vinyl ether, butylamino ethyl vinyl ether, benzyl vinyl ether, tetrahydrofurfuryl vinyl ether, etc.;

[0236] Vinyl ester, for example, vinyl butyrate, vinyl iso butyrate, vinyl trimethyl acetate, vinyl diethyl acetate, vinyl BARETO, vinyl caproate, vinyl KURORU acetate, vinyl dichloro acetate, vinyl methoxy acetate, vinyl butoxy acetate, vinyl acetoacetate, vinyl lactate, vinyl-beta-phenyl butyrate, vinyl cyclohexyl carboxylate, etc.;

[0237] Itaconic-acid dialkyls (for example, dimethyl itaconate, itaconic-acid diethyl, dibutyl itaconate, etc.); there are an acrylic acid, a methacrylic acid, a crotonic acid, an itaconic acid, acrylonitrile, a methacrylonitrile, etc.

[0238] The rate of each repeat unit can take into consideration the dry etching resistance of a desired resist, sensibility, cracking prevention of a pattern, substrate adhesion, a resist profile, the resolution that is the requisite of a still more general resist, thermal resistance, etc., and can set them up suitably.

[0239] the content of the repeat structural unit shown by the general formula in acidolysis nature resin (I) — all inside of repeat structural unit, 10 – 60-mol % — desirable — more — desirable — 15 – 55-mol % — it is 20 – 50-mol % still more preferably. the content of the repeat structural unit shown by the general formula

(II) among acidolysis nature resin -- all 10 in repeat structural unit -- 70-mol % -- desirable -- more -- desirable -- 15 - 60-mol % -- it is 20 - 50-mol % still more preferably. the content of the repeat structural unit shown by the general formula (III) among acidolysis nature resin -- all inside of repeat structural unit, and 2-50-mol % -- desirable -- more -- desirable -- 4-45-mol % -- it is 6-40-mol % still more preferably. [0240] Among acidolysis nature resin, 15 - 90-mol % is desirable, and is 15 - 85-mol % more preferably, and the sum total of the repeat unit which has acidolysis nature machines, such as a general formula (I) and (III) a repeat structural unit shown, is 20 - 80-mol % still more preferably.

[0241] Moreover, although the content in the resin of the repeat structural unit based on the monomer of further copolymerization components other than the above (I), (II), or (III) the repeat structural unit shown can also be suitably set up according to the engine performance of a desired resist As opposed to the total number of mols which generally totaled a general formula (I), (II), and (III) the repeat structural unit shown As for the mol number which totaled other further repeat structural units, less than [ 99 mol % ] is desirable, and it is less than [ 80 mol % ] preferably [ it is more desirable and ] to a 90 mol % less or equal and a pan. Moreover, when the constituent of this invention is an object for ArF exposure, as for the point of transparency over ArF light to acidolysis nature resin, it is desirable that an aromatic series ring is not included.

[0242] The acidolysis nature resin used for this invention is compoundable according to a conventional method (for example, radical polymerization). For example, as the general composition approach, are a package or a monomer kind is taught to a reaction container in the middle of a reaction. The need is accepted in this. A reaction solvent, for example, a tetrahydrofuran, 1,4-dioxane, Ether, such as diisopropyl ether, and the ketones like a methyl ethyl ketone and methyl isobutyl ketone After making it dissolve in an ester solvent like ethyl acetate, and the solvent which dissolves the constituent of this invention like the further below-mentioned propylene-glycol-monomethyl-ether acetate and considering as homogeneity, A polymerization is made to start using the radical initiators (an azo system initiator, peroxide, etc.) of heating and marketing if needed under inert gas ambient atmospheres, such as nitrogen and an argon. An initiator is added by an addition or division by request, after reaction termination, it supplies to a solvent and desired polymers are collected by approaches, such as fine particles or solid recovery. The concentration of a reaction is 20 % of the weight or more, and is 40 % of the weight or more still more preferably 30% of the weight or more preferably. Reaction temperature is 10 degrees C - 150 degrees C, and is 50-100 degrees C still more preferably 30 degrees C - 120 degrees C preferably.

[0243] The weight average molecular weight of the acidolysis nature resin concerning this invention is 1,000-200,000 preferably as a polystyrene reduced property by the GPC method. Since development nature will deteriorate or viscosity will become very high if weight average molecular weight exceeds 200,000 not much preferably, since degradation of thermal resistance or dry etching resistance is seen less than by 1,000, the result which is not not much desirable -- film production nature deteriorates -- is produced.

[0244] In the positive type photoresist constituent for far-ultraviolet-rays exposure of this invention, among [ all ] resist solid content, the loadings in the whole constituent of the acidolysis nature resin concerning this invention have 40 - 99.99 desirable % of the weight, and are 50 - 99.97 % of the weight more preferably.

[0245] It is desirable to dissolve solid content, such as the above-mentioned (A) photo-oxide generating agent and (B) resin, in the above-mentioned solvent three to 25% of the weight as solid content

concentration, and it is 7 – 20 % of the weight still more preferably five to 22% of the weight more preferably.

[0246] [3] The positive type photoresist constituent of (C) partially aromatic solvent this invention contains a partially aromatic solvent as a (C) component. As this partially aromatic solvent, the partially aromatic solvent which contains at least one sort (it is also called the solvent of B group) and/or gamma-butyrolactone, ethylene carbonate, and propylene carbonate (it is also called the solvent of C group) among propylene glycol monoalkyl ether carboxylate among at least one sort (it is also called the solvent of A group), propylene glycol monoalkyl ether and lactic-acid alkyl, and alkoxy propionic-acid alkyl can be mentioned. That is, as a (C) component, the combination of the solvent of A group and the solvent of B group, the combination of the solvent of A group and the solvent of C group, and the combination of the solvent of A group, the solvent of B group, and the solvent of C group are used. If the combination of the solvent of A group and the solvent of B group is used, sensibility will be excelled in resolving of a contact hole and early particle generating in resist liquid will be improved. An increment and sensibility fluctuation of particle are controlled by the passage of time of resist liquid by the combination of the solvent of A group, and the solvent of C group, and the resist excellent in stability with the passage of time is obtained. As propylene glycol monoalkyl ether carboxylate, propylene-glycol-monomethyl-ether acetate, propylene-glycol-monomethyl-ether propionate, propylene glycol monoethyl ether acetate, and propylene glycol monoethyl ether propionate can be mentioned preferably.

[0247] As propylene glycol monoalkyl ether, propylene glycol monomethyl ether and the propylene glycol monoethyl ether can be mentioned preferably. As lactic-acid alkyl, methyl lactate and ethyl lactate can be mentioned preferably. As alkoxy propionic-acid alkyl, 3-ethoxy ethyl propionate, 3-methoxy methyl propionate, 3-methoxy ethyl propionate, and 3-ethoxy methyl propionate can be mentioned preferably.

[0248] 90:10–15:85 are desirable, and are 85:15–20:80 more preferably, and the operating weight ratios (A:B) of the solvent of the above-mentioned A group and the solvent of B group are 80:20–25:75 still more preferably. 99.9:0.1–75:25 are desirable, and are 99:1–80:20 more preferably, and the operating weight ratios (A:C) of the solvent of the above-mentioned A group and the solvent of C group are 97:3–85:15 still more preferably.

[0249] When combining three sorts of these solvents, the operating weight ratio of the solvent of C group has 0.1 – 25 desirable % of the weight to all solvents, and is 3 – 17 % of the weight still more preferably one to 20% of the weight more preferably. In this invention, it is desirable to dissolve the solid content of the resist constituent containing each above-mentioned component in the above-mentioned partially aromatic solvent three to 25% of the weight as solid content concentration, it is 5 – 22 % of the weight more preferably, and is 7 – 20 % of the weight still more preferably.

[0250] As a desirable combination of the partially aromatic solvent containing the propylene glycol monoalkyl ether carboxylate in this invention Propylene-glycol-monomethyl-ether acetate + propylene-glycol-monomethyl-ether propylene-glycol-monomethyl-ether acetate + ethyl lactate propylene-glycol-monomethyl-ether acetate +3-ethoxyethyl PUROPIONETOPUROPURENGURIKO RUMONO methyl ether acetate + gamma-butyrolactone propylene-glycol-monomethyl-ether acetate + ethylene carbonate propylene-glycol-monomethyl-ether acetate + propylene carbonate propylene-glycol-monomethyl-ether acetate + PUROPI RENGU recall monomethyl ether + gamma-butyrolactone propylene-glycol-monomethyl-ether acetate + ethyl lactate + gamma-butyrolactone

propylene-glycol-monomethyl-ether acetate + 3-ethoxyethyl propionate + gamma-butyrolactone pro  
PIRENGURI Call monomethyl ether acetate + propylene-glycol-monomethyl-ether + ethylene carbonate  
propylene-glycol-monomethyl-ether acetate + ethyl lactate + ethylene carbonate  
propylene-glycol-monomethyl-ether acetate +3-ethoxy ECHIRUPU ROPIONETO + ethylene carbonate  
propylene-glycol-monomethyl-ether acetate + propylene-glycol-monomethyl-ether + propylene carbonate  
propylene glycol MONOME It is chill ether acetate + ethyl lactate + propylene carbonate  
propylene-glycol-monomethyl-ether acetate + 3-ethoxyethyl propionate + propylene carbonate.

[0251] As a combination of a desirable solvent, especially Propylene-glycol-monomethyl-ether acetate +  
propylene-glycol-monomethyl-ether + gamma-butyrolactone propylene-glycol-monomethyl-ether acetate  
+ ethyl lactate + gamma-butyrolactone propylene-glycol-monomethyl-ether acetate +3-ETOKI SHIECHIRU  
propionate + gamma-butyrolactone propylene-glycol-monomethyl-ether acetate +  
propylene-glycol-monomethyl-ether + ethylene carbonate propylene-glycol-monomethyl-ether acetate +  
ethyl lactate + ethylene carbonate pro PIRENGURI Call monomethyl ether acetate + 3-ethoxyethyl  
propionate + ethylene carbonate propylene-glycol-monomethyl-ether acetate +  
propylene-glycol-monomethyl-ether + propylene car BONE It is TOPUROPURENGURIKORU monomethyl  
ether acetate + ethyl lactate + propylene carbonate propylene-glycol-monomethyl-ether acetate +  
3-ethoxyethyl propionate + propylene carbonate.

[0252] Moreover, as a (C) component of this invention, it is a partially aromatic solvent containing at least  
one sort (it is also called the solvent of (1)), and at least one sort in an ester solvent and alkoxy  
propionic-acid alkyl in lactic-acid alkyl (it is also called the solvent of (2)). Sensibility is excelled in resolving  
of a contact hole and early particle generating in resist liquid is improved by addition of the solvent of (2) to  
the solvent of (1). As lactic-acid alkyl, methyl lactate and ethyl lactate can be mentioned preferably.

[0253] As an ester solvent, butyl acetate, pentyl acetate, acetic-acid hexyl, and butyl propionate can be  
mentioned preferably, and it is butyl acetate more preferably. As alkoxy propionic-acid alkyl, 3-ethoxy ethyl  
propionate, 3-methoxy methyl propionate, 3-methoxy ethyl propionate, and 3-ethoxy methyl propionate can  
be mentioned preferably.

[0254] 90:10-15:85 are desirable, and are 85:15-20:80 more preferably, and the operating weight ratios ((1) :  
(2)) of the solvent of the above (1) and the solvent of (2) are 80:20-25:75 still more preferably.

[0255] In this invention, it is desirable to contain at least one sort in gamma-butyrolactone, ethylene  
carbonate, and propylene carbonate (for it to also be called the solvent of (3)) further in the partially  
aromatic solvent of (C). By adding the solvent of (3), an increment and sensibility fluctuation of particle are  
controlled by the passage of time of resist liquid, and the resist excellent in stability with the passage of time  
is obtained. The operating weight ratio of the solvent of (3) has 0.1 - 25 desirable % of the weight to all  
solvents, and its 1 - 20 % of the weight is more desirable, and it is 3 - 15% more preferably. In this invention,  
it is desirable to dissolve the solid content of the resist constituent containing each above-mentioned  
component in the above-mentioned partially aromatic solvent three to 25% of the weight as solid content  
concentration, it is 5 - 22 % of the weight more preferably, and is 7 - 20 % of the weight still more preferably.

[0256] As a desirable combination of the partially aromatic solvent containing the lactic-acid alkyl in this  
invention Ethyl lactate + butyl-acetate and ethyl lactate + butyl-acetate + gamma-butyrolactone, Ethyl  
lactate + butyl-acetate + ethylene carbonate, ethyl lactate + butyl-acetate + propylene carbonate, Ethyl



lactate +3-ethoxy ethyl propionate + gamma-butyrolactone, Ethyl lactate +3-ethoxy ethyl propionate + ethylene carbonate, Ethyl lactate +3-ethoxy ethyl propionate + propylene carbonate is mentioned. Preferably Furthermore, ethyl lactate + butyl-acetate + gamma-butyrolactone, ethyl lactate + butyl-acetate + ethylene carbonate, Ethyl lactate + butyl-acetate + propylene carbonate, ethyl lactate +3-ethoxy ethyl propionate + gamma-butyrolactone, They are ethyl lactate +3-ethoxy ethyl propionate + ethylene carbonate and ethyl lactate +3-ethoxy ethyl propionate + propylene carbonate.

[0257] Furthermore, as a (C) component of this invention, it is the solvent which contains at least one sort (it is also called the solvent of (5)), and heptanone (it is also called the solvent of (4)) among propylene glycol monoalkyl ether, lactic-acid alkyl, and alkoxy propionic-acid alkyl. Thereby, sensibility is excelled in resolving of a contact hole and early particle generating in resist liquid is improved. As heptanone, 2-heptanone, 3-heptanone, and 4-heptanone can be mentioned, and it is 2-heptanone preferably.

[0258] As propylene glycol monoalkyl ether, propylene glycol monomethyl ether and the propylene glycol monoethyl ether can be mentioned preferably. As lactic-acid alkyl, methyl lactate and ethyl lactate can be mentioned preferably. As alkoxy propionic-acid alkyl, 3-ethoxy ethyl propionate, 3-methoxy methyl propionate, 3-methoxy ethyl propionate, and 3-ethoxy methyl propionate can be mentioned preferably.

[0259] The amount of the solvent used of the above (4) is usually 30 % of the weight or more to all solvents, and is 50 % of the weight or more more preferably 40% of the weight or more. The amount of the solvent used of (5) is usually 5 - 70 % of the weight to all solvents, and is 15 - 50 % of the weight more preferably ten to 60% of the weight. Since the problem of spreading nature deteriorating may arise if the addition effectiveness falls if there is less amount of the solvent used of (5) than the above-mentioned range, and 70 % of the weight is exceeded, it is not desirable.

[0260] In this invention, it is desirable to contain at least one sort in gamma-butyrolactone, ethylene carbonate, and propylene carbonate (for it to also be called the solvent of (6)) further in the solvent of (C). By adding the solvent of (6), an increment and sensibility fluctuation of particle are controlled by the passage of time of resist liquid, and the resist excellent in stability with the passage of time is obtained. The operating weight ratio of the solvent of (6) has 0.1 - 25 desirable % of the weight to all solvents, and its 1 - 20 % of the weight is more desirable, and it is 3 - 15% more preferably. In this invention, it is desirable to dissolve the solid content of the resist constituent containing each above-mentioned component in the above-mentioned partially aromatic solvent three to 25% of the weight as solid content concentration, it is 5 - 22 % of the weight more preferably, and is 7 - 20 % of the weight still more preferably.

[0261] As a desirable combination of the partially aromatic solvent containing the heptanone in this invention 2-heptanone + propylene glycol monomethyl ether, 2-heptanone + ethyl lactate, 2-heptanone +3-ethoxy ethyl propionate, 2-heptanone + gamma-butyrolactone, 2-heptanone + ethylene carbonate, 2-heptanone + propylene carbonate, 2-heptanone + propylene-glycol-monomethyl-ether + gamma-butyrolactone, 2-heptanone + ethyl lactate + gamma-butyrolactone, 2-heptanone +3-ethoxy ethyl propionate + gamma-butyrolactone, 2-heptanone + propylene-glycol-monomethyl-ether + ethylene carbonate, 2-heptanone + ethyl lactate + ethylene carbonate, 2-heptanone +3-ethoxy ethyl propionate + ethylene carbonate, They are 2-heptanone + propylene-glycol-monomethyl-ether + propylene carbonate, 2-heptanone + ethyl lactate + propylene carbonate, and 2-heptanone +3-ethoxy ethyl propionate + propylene carbonate. Still more preferably 2-heptanone + propylene-glycol-monomethyl-ether +

gamma-butyrolactone, 2-heptanone + ethyl lactate + gamma-butyrolactone, 2-heptanone +3-ethoxy ethyl propionate + gamma-butyrolactone, 2-heptanone + propylene-glycol-monomethyl-ether + ethylene carbonate, 2-heptanone + ethyl lactate + ethylene carbonate, 2-heptanone +3-ethoxy ethyl propionate + ethylene carbonate, They are 2-heptanone + propylene-glycol-monomethyl-ether + propylene carbonate, 2-heptanone + ethyl lactate + propylene carbonate, and 2-heptanone +3-ethoxy ethyl propionate + propylene carbonate.

[0262] Each above-mentioned partially aromatic solvent of this invention may add other solvents which are not indispensable in the range which does not bar the effectiveness of this invention. Generally the addition of such other solvents is below 30 weight sections to each partially aromatic solvent 100 weight section of this invention. In addition to the solvent illustrated as an indispensable solvent, as other solvents, ethylene dichloride, a cyclohexanone, cyclopentanone, a methyl ethyl ketone, toluene, N.N-dimethylformamide, dimethyl sulfoxide, N-methyl pyrrolidone, a tetrahydrofuran, etc. can be mentioned to each above-mentioned partially aromatic solvent.

[0263] [4] As for the positive type photoresist constituent for far-ultraviolet-rays exposure of surface-active-agent this invention, it is desirable to contain a fluorine system and/or a silicon system surface active agent. As a fluorine system and/or a silicon system surfactant, they are at least one sort of surfactants of the surfactant containing both a fluorochemical surfactant, a silicon system surfactant and a fluorine atom, and a silicon atom. When the positive type photoresist constituent for far-ultraviolet-rays exposure of this invention contains the above-mentioned acidolysis nature resin and the above-mentioned surfactant, especially, sensibility, resolving power, substrate adhesion, and dry etching-proof nature are excellent at the time of use of the exposure light source 220nm or less, and 250nm or less of resist patterns with still less a development defect and Society for Cutting Up Men is obtained at it. As these surfactants, for example, JP,62-36663,A, JP,61-226746,A, JP,61-226745,A, JP,62-170950,A, JP,63-34540,A, JP,7-230165,A, JP,8-62834,A, JP,9-54432,A, JP,9-5988,A, a U.S. Pat. No. 5405720 number, said 5360692 numbers, said -- No. 5529881 -- said -- No. 5296330 -- said -- No. 5436098 -- said -- No. 5576143 -- said -- a surfactant No. 5294511 and given [ this ] in No. 5824451 can be mentioned, and the surfactant of the following marketing can also be used as it is. As a surfactant of marketing which can be used, a fluorochemical surfactant or silicon system surfactants, such as EFUTOPPU EF301 and EF303, (made in new Akita Chemicals), Fluorad 430 and FC 431 (Sumitomo 3M make), the megger fucks F171, F173, F176, F189, and R08 (Dainippon Ink & Chemicals, Inc. make), Sir chlorofluocarbon S-382, and SCs 101, 102, 103, 104, 105, and 106 (Asahi Glass Co., Ltd. make), can be mentioned. Moreover, polysiloxane polymer KP-341 (Shin-Etsu Chemical Co., Ltd. make) can be used as a silicon system surfactant.

[0264] The loadings of a surfactant are usually 0.01 % of the weight - 1 % of the weight preferably on the basis of the solid content in the constituent of this invention 0.001 % of the weight to 2% of the weight. these surfactants are one-sort independent -- it is -- it can use combining two or more sorts.

[0265] As a surface active agent besides the above, specifically The polyoxyethylene lauryl ether, Polyoxyethylene stearylether, the polyoxyethylene cetyl ether, Polyoxyethylene alkyl ether, such as the polyoxyethylene oleyl ether Polyoxyethylene alkyl aryl ether, such as the polyoxyethylene octyl phenol ether and the polyoxyethylene nonyl phenol ether Polyoxyethylene polyoxypropylene block copolymers Sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, Sorbitan fatty acid esters, such as sorbitan

monooleate, sorbitan trioleate, and sorbitan tristearate Polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, The Nonion system surfactants, such as polyoxyethylene sorbitan fatty acid ester, such as polyoxyethylenesorbitan monostearate, polyoxyethylene sorbitan trioleate, and polyoxyethylene sorbitan tristearate, etc. can be mentioned. The loadings of these surfactants are usually below 1 weight section preferably below 2 weight sections per solid content 100 weight section in the constituent of this invention. You may add independently and these surfactants can also be added in some combination.

[0266] [5] The desirable organic base nature compound which can be used by organic base nature compound this invention is a compound with basicity stronger than a phenol. A nitrogen-containing basicity compound is desirable especially.

[0267]

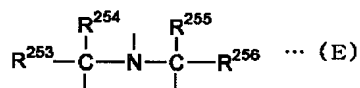
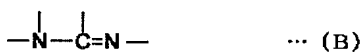
[Formula 112]



[0268] It is the permutation or the unsubstituted aryl group of that R250, R251, and R252 are the same, or a difference, a hydrogen atom, the alkyl group of carbon numbers 1–6, the amino alkyl group of carbon numbers 1–6, the hydroxyalkyl radical of carbon numbers 1–6 or carbon numbers 6–20, and it may join together mutually and R251 and R252 may form a ring here.

[0269]

[Formula 113]



[0270] (R253, R254, R255, and R256 show the alkyl group of the same, or a difference and carbon numbers 1–6 among a formula)

Furthermore, a desirable compound is a nitrogen-containing basicity compound which has two or more nitrogen atoms of different chemical environment in a monad, and is a compound which has especially a compound or alkylamino radical including both ring structures containing the amino group and nitrogen atom which are not permuted [ a permutation or ] preferably. As a desirable example, the aminopyridine which is not permuted [ the guanidine which is not permuted / a permutation or / a permutation, or ], The amino pyrrolidine which is not permuted [ the amino alkyl pyridine which is not permuted / a permutation or / a permutation, or ], The pyrazole which is not permuted [ in DAZORU which is not permuted / a permutation or /, a permutation or ], The pyrimidine which is not permuted [ the pyrazine which is not permuted / a

permutation or /, a permutation, or ], The amino alkyl morpholine which is not permuted [ the amino morpholine which is not permuted / the piperazine which is not permuted / the pyrazoline which is not permuted / the imidazoline which is not permuted / the pudding which is not permuted / a permutation or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or ] is mentioned. Desirable substituents are the amino group, an amino alkyl group, an alkylamino radical, an amino aryl group, an arylamino radical, an alkyl group, an alkoxy group, an acyl group, an acyloxy radical, an aryl group, an aryloxy group, a nitro group, a hydroxyl group, and a cyano group.

[0271] As a desirable concrete compound, guanidine, 1, and 1-dimethyl guanidine, 1, 1, 3, 3, - tetramethyl guanidine, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 2-dimethylamino pyridine, 4-dimethylaminopyridine, 2-diethylamino pyridine, 2-(aminomethyl) pyridine, 2-amino-3-methylpyridine, 2-amino-4-methylpyridine, 2-amino-5-methylpyridine, 2-amino-6-methylpyridine, 3-aminoethyl pyridine, 4-aminoethyl pyridine, 3-amino pyrrolidine, A piperazine, N-(2-aminoethyl) piperazine, N-(2-aminoethyl) piperidine, 4-amino - 2, 2, 6, and 6-tetramethylpiperidine, 4-piperidino piperidine, A 2-imino piperidine, 1-(2-aminoethyl) pyrrolidine, a pyrazole, 3-amino-5-methyl pyrazole, 5 - Amino-3-methyl-1-p-tolyl pyrazole, Pyrazine, 2-(aminomethyl)-5-methyl pyrazine, a pyrimidine, 2, 4-diamino pyrimidine, 4, 6-dihydroxy pyrimidine, 2-pyrazoline, 3-pyrazoline, N-amino morpholine, N-(2-aminoethyl) morpholine, 1, a 5-diazabicyclo [4, 3, 0] nona-5-en, 1, a 8-diazabicyclo [5, 4, 0] undeca-7-en, 2, 4, 5-triphenyl imidazole, N-methyl morpholine, N-ethyl morpholine, The 3rd class morpholine derivatives, such as N-hydroxyethyl morpholine, N-benzyl morpholine, and cyclohexyl morpholino ethyl thiourea (CHMETU), Although the hindered amine (for example, thing given in this official report [0005]) of a publication is mentioned to JP,11-52575,A, it is not limited to this.

[0272] Especially a desirable example 1, 5-diazabicyclo [4.3.0]-5-nonene, 1, 8-diazabicyclo [5.4.0]-7-undecene, 1, 4-diazabicyclo [2.2.2] octane, 4-dimethylaminopyridine, hexamethylenetetramine, 4, and 4-dimethyl imidazoline, Hindered amine, such as the 3rd class morpholines, such as pyrroles, pyrazoles, imidazole derivatives, pyridazines, pyrimidines, and CHMETU, and bis(1, 2, 2, 6, and 6-pentamethyl-4-piperidyl) SEBAGETO, can be mentioned. By using these, a dependency of condensation and rarefaction comes to be excellent.

[0273] Especially, 1, 5-diazabicyclo [4, 3, 0] nona-5-en, 1, 8-diazabicyclo [5, 4, 0] undeca-7-en, 1, and 4-diazabicyclo [2, 2, 2] octane, 4-dimethylaminopyridine, a hexamethylenetetramine, CHMETU, and bis(1, 2, 2, 6, and 6-pentamethyl-4-piperidyl) SEBAGETO are desirable.

[0274] These nitrogen-containing basicity compounds are independent, or are combined two or more sorts and used. The amount of the nitrogen-containing basicity compound used is usually 0.01 - 5 % of the weight preferably 0.001 to 10% of the weight to the solid content of all the constituents of a photopolymer constituent. At less than 0.001 % of the weight, the effectiveness of addition of the above-mentioned nitrogen-containing basicity compound is not acquired. On the other hand, when it exceeds 10 % of the weight, there is an inclination for the development nature of the fall of sensibility or a non-exposed area to get worse.

[0275] [6] The positive type photoresist constituent of other additive this inventions can be made to contain the compound which promotes the solubility over an acidolysis nature lysis inhibition compound, a color, a plasticizer, a sensitizer, and a developer further if needed.

[0276] Such a positive type photoresist constituent of this invention is applied on a substrate, and forms a thin film. The thickness of this paint film has desirable 0.2–1.2 micrometers. In this invention, inorganic [ commercial ] or an organic antireflection film can be used as occasion demands.

[0277] As antireflection film, inorganic membrane types, such as titanium, a titanium dioxide, titanium nitride, chromic oxide, carbon, and alpha-silicon, and the organic membrane type which consists of an extinction agent and a polymer ingredient can use. The former needs a facility of a vacuum evaporation system, a CVD system, a sputtering system, etc. for film formation. As organic antireflection film, for example The condensation product of a diphenylamine derivative given in JP,7-69611,B, and formaldehyde denaturation melamine resin, The thing, the maleic-anhydride copolymer given in U.S. Pat. No. 5294680, and the reactant of a diamine mold extinction agent which consist of alkali fusibility resin and an extinction agent, The thing containing a resin binder given in JP,6-118631,A, and a methylol melamine system heat cross linking agent, The acrylic resin mold antireflection film which has a carboxylic-acid radical, an epoxy group, and an extinction radical given in JP,6-118656,A in the same intramolecular, What consists of a methylol melamine given in JP,8-87115,A and a benzophenone system extinction agent, the thing which added the low-molecular extinction agent to polyvinyl alcohol resin given in JP,8-179509,A are mentioned. Moreover, DUV30 series by BURYUWA Saiensu-Sha, AC-2 of DUV-40 series and the product made from SHIPURE, AC-3, etc. can also be used as organic antireflection film.

[0278] On a substrate (example: silicon / diacid-ized silicon covering) which is used for manufacture of a precision integrated circuit device, the above-mentioned resist liquid can be exposed through a predetermined mask after spreading by the suitable methods of application, such as a spinner and a coating machine, (on the substrate which was able to prepare the above-mentioned antireflection film as occasion demands), and a good resist pattern can be obtained by developing negatives by performing BEKU. As an exposure light, it is light with a wavelength of 150nm – 250nm preferably here. Specifically, a KrF excimer laser (248nm), an ArF excimer laser (193nm), F2 excimer laser (157nm), an X-ray, an electron beam, etc. are mentioned.

[0279] As a developer, a sodium hydroxide, a potassium hydroxide, a sodium carbonate, Inorganic alkali, such as a sodium silicate, a meta-sodium silicate, and aqueous ammonia Primary amines, such as ethylamine and n propylamine, diethylamine, Tertiary amines, such as secondary amines, such as G n butylamine, triethylamine, and methyl diethylamine Alcoholic amines, such as dimethylethanolamine and triethanolamine, Alkaline water solutions, such as annular amines, such as quarternary ammonium salt, such as tetramethylammonium hydroxide and tetraethylammonium hydroxide, a pyrrole, and PIHERIJIN, can be used. Furthermore, alcohols and a surfactant can also be used for the alkaline above-mentioned water solution, carrying out suitable amount addition.

[0280]

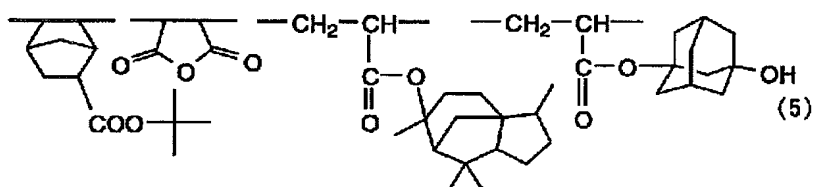
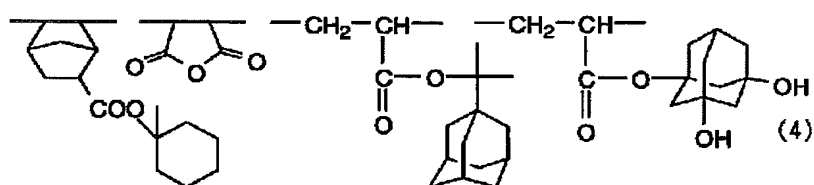
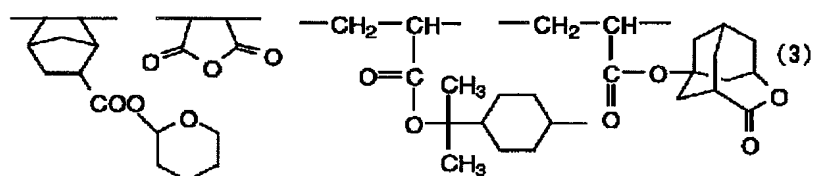
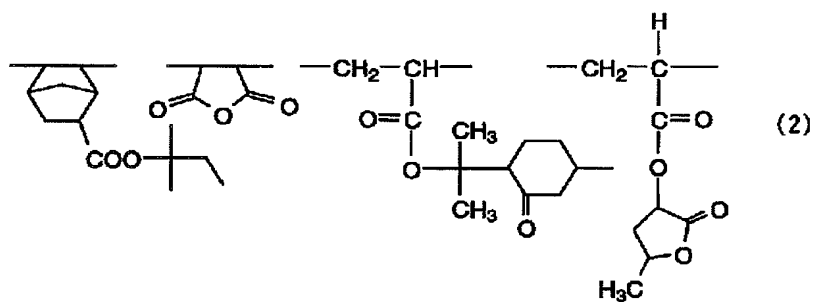
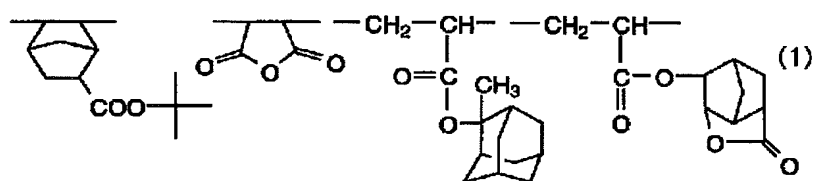
[Example] Hereafter, although an example explains this invention still more concretely, this invention is not limited to the following examples.

[0281] [Composition of acidolysis nature resin] Norbornene carboxylic-acid t butyl ester, a maleic anhydride, 2-methyl-2-adamantyl acrylate, and norbornene lactone acrylate were taught to the reaction container by the mole ratio 20/20/35/25, it dissolved in a methyl ethyl ketone / tetrahydrofuran =1/1 solvent, and the solution of 60% of solid content was prepared. This was heated at 65 degrees C under the nitrogen air

current. the place by which reaction temperature was stabilized -- the Wako Pure Chem radical initiator V-601 -- three-mol% -- the reaction was made to start in addition After heating for 12 hours, the reaction mixture was thrown into the hexane of an amount 5 times, and white fine particles were deposited. The fine particles which deposited were again dissolved in the methyl-ethyl-ketone / tetrahydrofuran =1/1 solvent, it supplied to the hexane / methyl tBu ether of the amount of 5 times, white fine particles were deposited, and it took out filtration picking. This activity was repeated again and the resin (1) which is desiccation and the specified substance was obtained. When the molecular-weight analysis (RI analysis) by GPC of the obtained resin (1) was tried, the amount of 11600 (weighted mean) and a residual monomer was 0.4% in polystyrene conversion. Moreover, the presentation of resin (1) was 18/23/34/25 in the mole ratio from the NMR spectrum about norbornene / maleic-anhydride / 2-methyl-2-adamantyl acrylate / norbornene lactone acrylate of this invention. Resin (2) - (25) was compounded by the same approach as the following. The structure of above-mentioned acidolysis nature resin (1) - (25) is shown below.

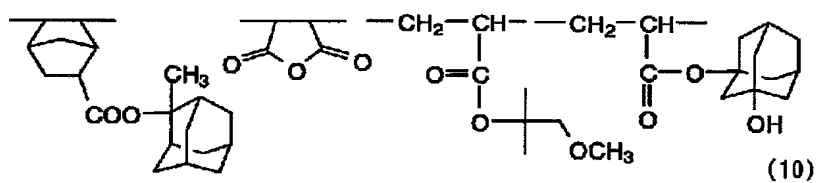
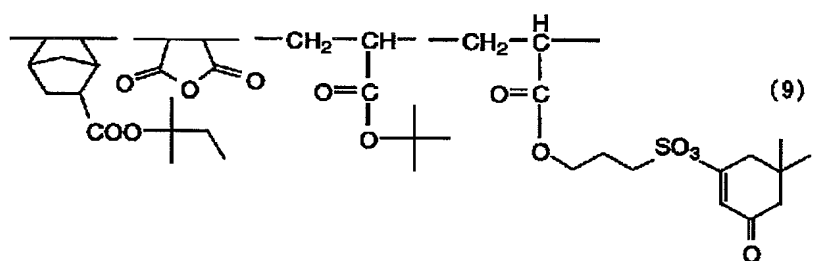
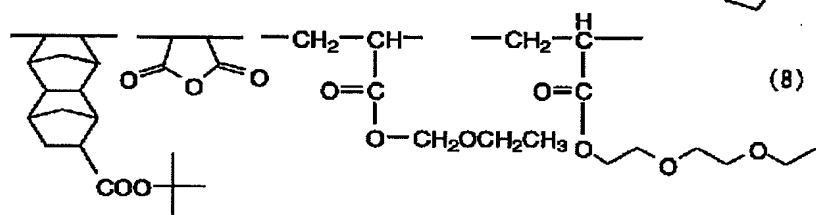
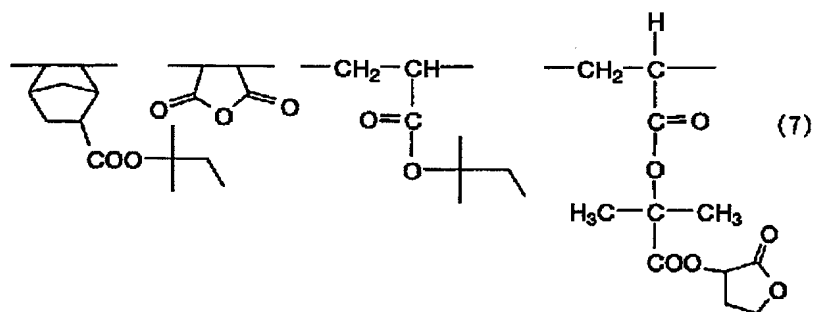
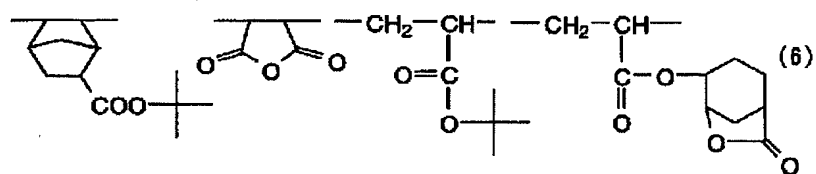
[0282]

[Formula 114]



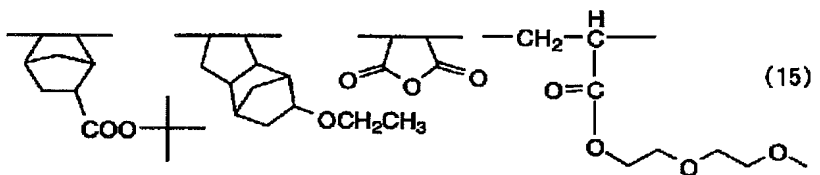
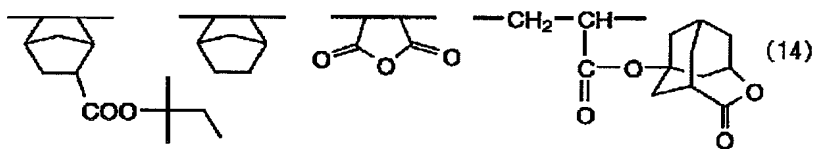
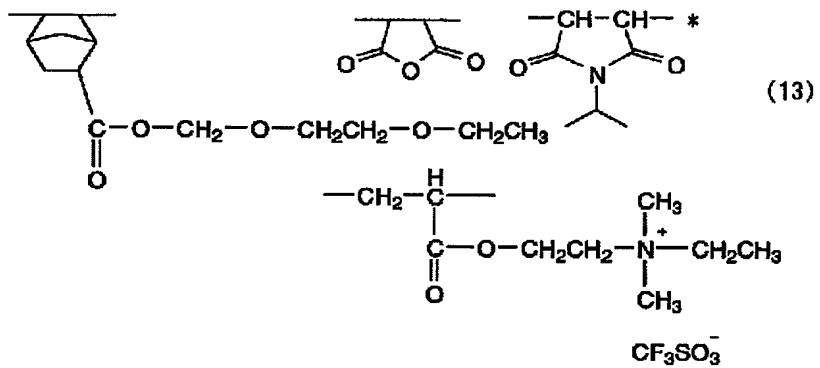
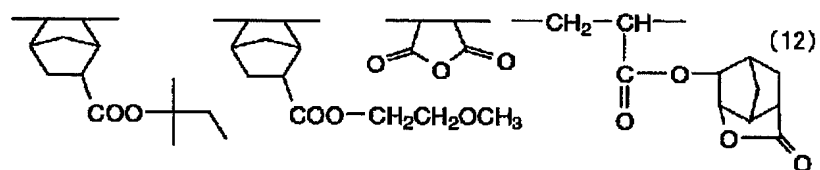
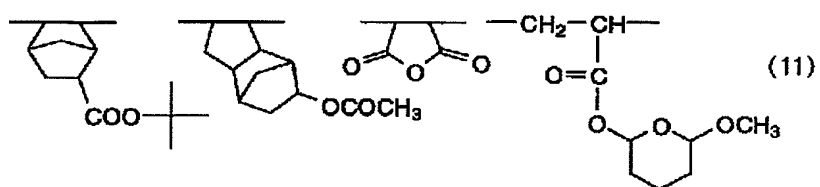
[0283]

[Formula 115]



[0284]

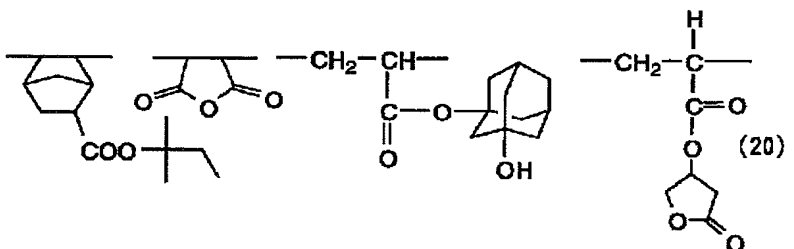
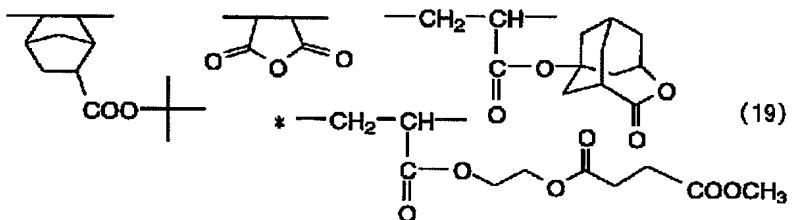
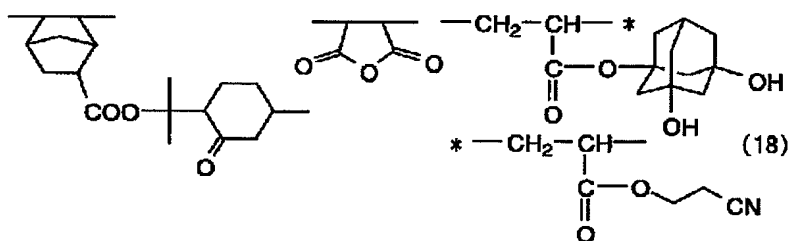
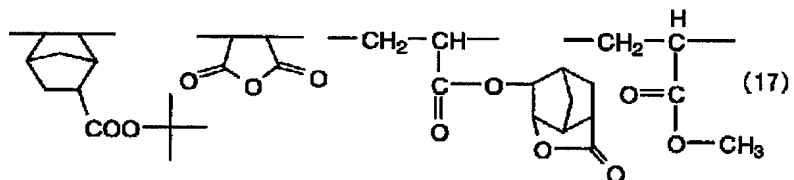
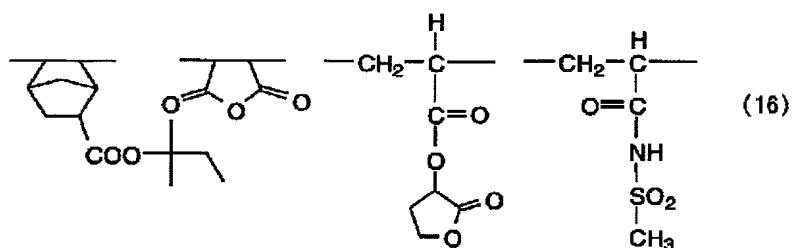
[Formula 116]



[0285]

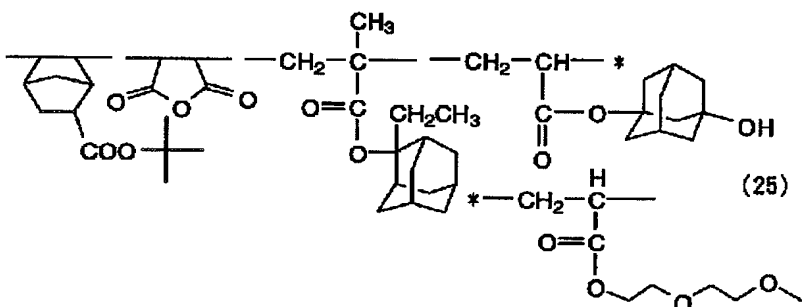
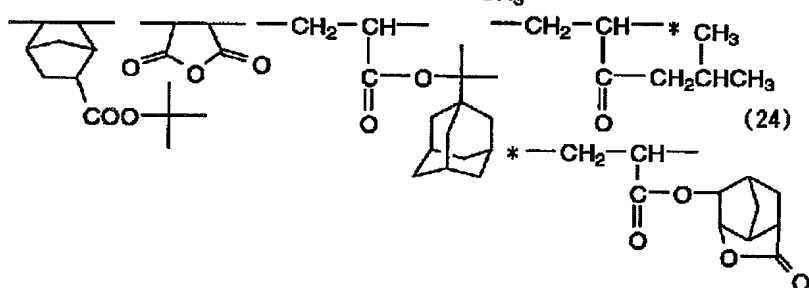
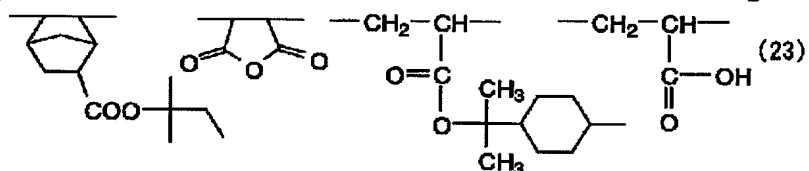
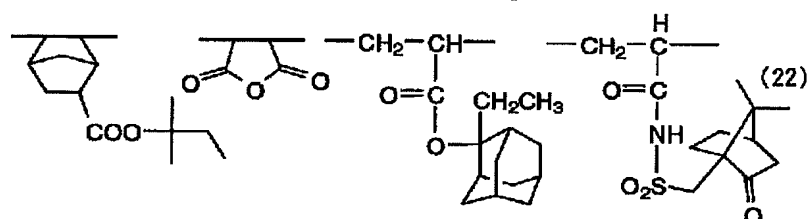
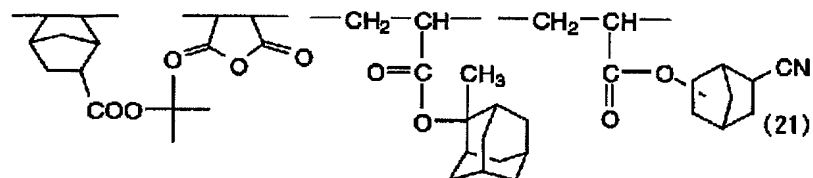
[Formula 117]





[0286]

[Formula 118]



[0287] Moreover, the mole fraction and weight average molecular weight of each repeat unit of above-mentioned acidolysis nature resin (1) - (25) are shown in Table 1.

[0288]

[Table 1]

表1

樹脂	脂環オレフィン	一般式(II)モノマー (無水物等)	アクリルモノマー	Mw
2	24	29	31/16	12300
3	21	28	32/29	11100
4	22	27	28/23	11300
5	27	31	24/18	10700
6	32	38	20/10	9700
7	31	35	21/13	9200
8	29	35	20/16	8900
9	35	39	23/3	8700
10	28	36	22/14	10600
11	28/8	44	20	9100
12	30/6	42	22	7700
13	46	47/3	4	6300
14	37/6	48	9	6800
15	34/10	51	5	7400
16	41	43	10/6	6700
17	39	42	11/8	8800
18	36	42	10/12	9300
19	39	43	14/4	9800
20	38	42	15/5	9300
21	24	27	25/24	12600
22	19	24	40/17	9500
23	29	32	34/5	10400
24	20	25	26/5/24	13400
25	16	24	32/24/4	12700

[0289] As shown in examples 1-40 and example of comparison 1 (preparation and evaluation of a positive type photoresist constituent) table 2 1.4g of acidolysis nature resin, the photo-oxide generating agent (the addition was shown in Table 2) which are shown in Table 1 compounded in the above-mentioned synthetic example, After blending 5mg of surfactants according to 4mg (amine) of organic base nature compounds, and the need and dissolving in a solvent at a rate of 14 % of the weight of solid content, respectively, it filtered by the 0.1-micrometer microfilter and the positive type photoresist constituent of the examples 1-40 shown in Table 2 was prepared. Moreover, the positive type photoresist constituent was prepared like the above-mentioned examples 1-40 as an example 1 of a comparison using the component shown in Table 2 containing comparison resin R.

[0290] Each compound in Table 2 is as follows.

[Solvent]

S1:propylene-glycol-monomethyl-ether acetate S2:ethyl lactate S3: -- butyl-acetate S4:2-heptanone S5:propylene-glycol-monomethyl-ether S6: -- ethoxy ethyl propionate S7:gamma-butyrolactone S8:ethylene carbonate S9: -- propylene carbonate [0291] [Surfactant]

W-1: Megger fuck F176 (Dainippon Ink & Chemicals, Inc. make) (fluorine system)

W-2: Megger fuck R08 (Dainippon Ink & Chemicals, Inc. make) (a fluorine and silicon system)

W-3: Polysiloxane polymer KP-341 (Shin-Etsu Chemical Co., Ltd. make)

W-4: Polyoxyethylene nonylphenyl ether W-5 : Troysol S-366 (made in Troy Chemical)

[0292] [Organic base nature compound]

1: DBU (1, 8-diazabicyclo [5.4.0]-7-undecene)

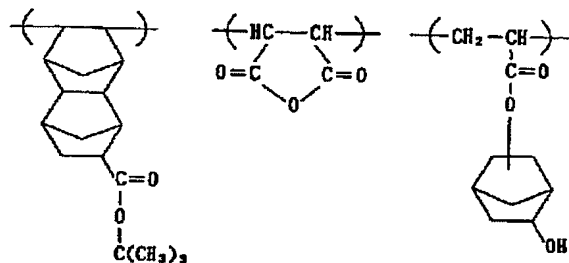
2:4-DMAP (4-dimethylaminopyridine)

3: TPI (2, 4, 5-triphenyl imidazole)

4:2, the 6-diisopropyl aniline 5:antipyrin 6: Tori n-octyl amine [0293] [Resin used in the example of a comparison]

Resin of the following structure used in the example 1 of resin R:EP 1048983A1 [0294]

[Formula 119]



[0295]

[Table 2]

表 2

実施例	樹脂	光酸発生剤	溶 剤	界面活性剤	有機塩基化合物
1	樹脂(1)	PAG3-23=42mg	S1/S7=90/10	W-5	1
2	樹脂(2)	PAG4-5/4-6=15/30mg	S1/S2=85/15	W-1	4
3	樹脂(3)	PAG4-26=33mg	S2/S6=80/20	W-3	5
4	樹脂(4)	PAG4-5=35mg	S4/S8=88/12	W-2	5
5	樹脂(5)	PAG4-7=34mg	S4/S5=85/15	W-1	4
6	樹脂(6)	PAG4-37=36mg	S2/S3=70/30	W-2	5
7	樹脂(7)	PAG4-5/4-36=10/30mg	S4/S9=80/20	W-3	4
8	樹脂(8)	PAG4-6=42mg	S1/S9=90/10	W-3	4
9	樹脂(9)	PAG4-38=45mg	S4/S7=85/15	W-5	3
10	樹脂(10)	PAG4-40=44mg	S4/S2=90/10	W-5	3
11	樹脂(11)	PAG4-5=37mg	S1/S5=88/12	-	-
12	樹脂(12)	PAG4-47=40mg	S4/S6=80/20	W-3	2
13	樹脂(13)	PAG4-36=40mg	S4のみ	-	5
14	樹脂(14)	PAG4-38=42mg	S1/S5/S8=80/17/3	W-1	2
15	樹脂(15)	PAG4-49=38mg	S1/S8=86/14	W-2	3
16	樹脂(16)	PAG4-5=38mg	S4/S8=80/20	W-3	-
17	樹脂(17)	PAG4-6=44mg	S2/S6/S7=65/30/5	W-4	4
18	樹脂(18)	PAG4-36=40mg	S1/S2/S7=78/18/4	W-5	5
19	樹脂(19)	PAG4-5=40mg	S4/S6/S9=65/30/5	W-2	4
20	樹脂(20)	PAG4-5=40mg	S1/S6/S9=80/15/5	W-1	3

[0296]

[Table 3]

表 2 (続き)

実施例	樹脂	光酸発生剤	溶 剤	界面活性剤	有機塩基化合物
21	樹脂(21)	PAG4-51=42mg	S1/S2/S7=80/13/7	W-1	6
22	樹脂(22)	PAG4-6=46mg	S2/S6/S8=60/30/10	W-1	1
23	樹脂(23)	PAG4-49=39mg	S2/S5/S8=75/15/10	W-2	3
24	樹脂(24)	PAG4-47=40mg	S4/S6/S7=60/30/10	W-3	4
25	樹脂(25)	PAG4-38=40mg	S1/S2/S8=75/21/4	W-3	5
26	樹脂(1)	PAG4-39/6-26=40/30mg	S4/S6/S9=70/20/10	W-5	3/5=1/1
27	樹脂(2)	PAG4-6/8-27=42/30mg	S2/S6/S9=65/28/7	W-5	3/5=1/1
28	樹脂(3)	PAG4-48/6-24=40/22mg	S4/S6/S8=55/40/5	W-3	4
29	樹脂(4)	PAG4-52/6-34=35/10mg	S1/S2/S9=85/10/5	W-1	4
30	樹脂(5)	PAG4-48/6-32=38/20mg	S1/S7=85/15	W-5	4/5=1/1
31	樹脂(6)	PAG4-51/6-19=35/20mg	S2/S3/S8=60/35/5	W-1	4
32	樹脂(7)	PAG4-47/7-3=40/15mg	S4/S2/S7=80/10/10	W-5	5
33	樹脂(8)	PAG4-5/7-5=38/12mg	S1/S5/S7=80/10/10	W-5	5
34	樹脂(9)	PAG4-38/6-26=30/20mg	S4/S6/S8=70/20/10	W-5	3
35	樹脂(10)	PAG4-37/6-27=32/15mg	S2/S3/S9=50/45/5	W-5	3/5=1/1
36	樹脂(21)	PAG4-36/6-24=40/25mg	S1/S5/S9=70/18/12	W-5	5
37	樹脂(22)	PAG4-39/6-26=30/10mg	S1/S8=90/10	W-3	5
38	樹脂(23)	PAG4-50/6-27=40/10mg	S2/S3/S7=48/47/5	W-1	5
39	樹脂(24)	PAG4-52/7-3=40/12mg	S4/S2/S8=80/12/8	W-1	3
40	樹脂(25)	PAG4-6/6-24=40/12mg	S1/S9=92/8	W-5	3
比較例					
1	樹脂(R)	PAG4-5=40mg	S4	-	6

[0297] (Evaluation trial) introduction Brewer Spreading [ use a spin coater for ARC-25 and ] of 30nm on a silicon wafer the product made from Science -- After drying, the positive type photoresist constituent obtained on it is applied. Desiccation and about 0.4-micrometer positive type photoresist film are created for 90 seconds at 130 degrees C. It exposed to it with the contact hole pattern (mask size of 0.16 microns) of 1/2 pitch with the ArF excimer laser (the wavelength of 193nm, ArF stepper by the ISI company of NA=0.6). Heat-treatment after exposure was performed for 90 seconds at 130 degrees C, the rinse was carried out with development and distilled water in 2.38% of the weight of the tetramethylammonium hydroxide water solution, and the resist pattern profile was obtained. Thus, the resist pattern of the obtained silicon wafer was observed under the scanning microscope, and the resist was evaluated as follows.

[0298] [Sensibility] The relative light exposure when making the minimum light exposure reproducing a :0.16micrometer contact hole into sensibility, and setting resist light exposure of an example 1 to 1.0 was expressed as relative sensibility (light exposure of the light exposure / example 1 of other resists).

[0299] [ -- the number of particle -- passing -- the time -- number of increments] of the particle after preservation -- : -- the number of particle in liquid after leaving it for one week at 4 degrees C immediately after preparation (particle initial value) about the positive type photoresist constituent solution (coating liquid) prepared as mentioned above (the number of particle after the passage of time) was counted at the Rion make and a particle counter. The number of the increments in particle calculated with particle initial value by - (the number of particle after the passage of time) (particle initial value) was evaluated. In addition, particle counted the number of the particle 0.25 micrometers or more in 1ml of resist constituent liquid.

[0300] [Sensibility fluctuation before and behind preservation with the passage of time]: The sensibility (light exposure after preservation) after doing in this way, and evaluating the sensibility (light exposure before preservation) immediately after preparation of a positive type photoresist constituent solution (coating liquid) and leaving the above-mentioned constituent solution for one week at 4 degrees C was evaluated, and the following type estimated sensibility rate of change.

sensibility rate-of-change (%) = \*\* (light exposure before preservation)-(light exposure after preservation) \*\* -- /(light exposure before preservation) x100 -- these evaluation results are shown in Table 3.

[0301]

[Table 4]

表 3

実施例	感度	感度変動率	パーティクル 初期値	パーティクル 増加数
1	1.0	5%	50	5
2	0.8	7%	30	10
3	0.8	7%	30	10
4	0.9	5%	40	5
5	0.8	8%	30	10
6	0.8	8%	30	10
7	0.9	6%	40	5
8	0.9	5%	40	5
9	0.9	6%	40	5
10	0.8	8%	30	10
11	0.9	10%	40	30
12	0.9	9%	40	20
13	1.0	12%	60	30
14	0.9	8%	40	10
15	1.0	8%	50	10
16	1.0	11%	55	20
17	0.9	8%	40	10
18	0.9	8%	40	10
19	0.9	9%	40	20
20	0.9	8%	40	10

[0302]

[Table 5]

表 3 (続き)

実施例	感度	感度変動率	パーティクル 初期値	パーティクル 増加数
21	0.8	4%	30	<5
22	0.8	4%	30	<5
23	0.8	4%	30	<5
24	0.8	4%	30	<5
25	0.8	4%	30	<5
26	0.6	4%	10	<5
27	0.8	4%	10	<5
28	0.6	4%	10	<5
29	0.6	4%	10	<5
30	0.7	5%	20	5
31	0.6	4%	10	<5
32	0.6	4%	10	<5
33	0.6	4%	10	<5
34	0.6	4%	10	<5
35	0.6	4%	10	<5
36	0.6	4%	10	<5
37	0.7	5%	20	5
38	0.6	4%	10	<5
39	0.6	4%	10	<5
40	0.7	5%	20	5
比較例 1	1.5	25%	55	270

[0303] As for the positive type photoresist constituent for ultraviolet-rays exposure concerning this invention, it turns out that sensibility, shelf life, and sensibility fluctuation are improved so that clearly from Table 3.

[0304]

[Effect of the Invention] In manufacture of a semiconductor device, this invention can offer the positive type photoresist constituent which can prevent generating of the particle at the time of melting solid content to a solvent, or the time of preservation with the passage of time, and can prevent fluctuation of the sensibility by preservation with the passage of time while having the sensibility which was excellent in resolving of a contact hole.

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[Translation done.]